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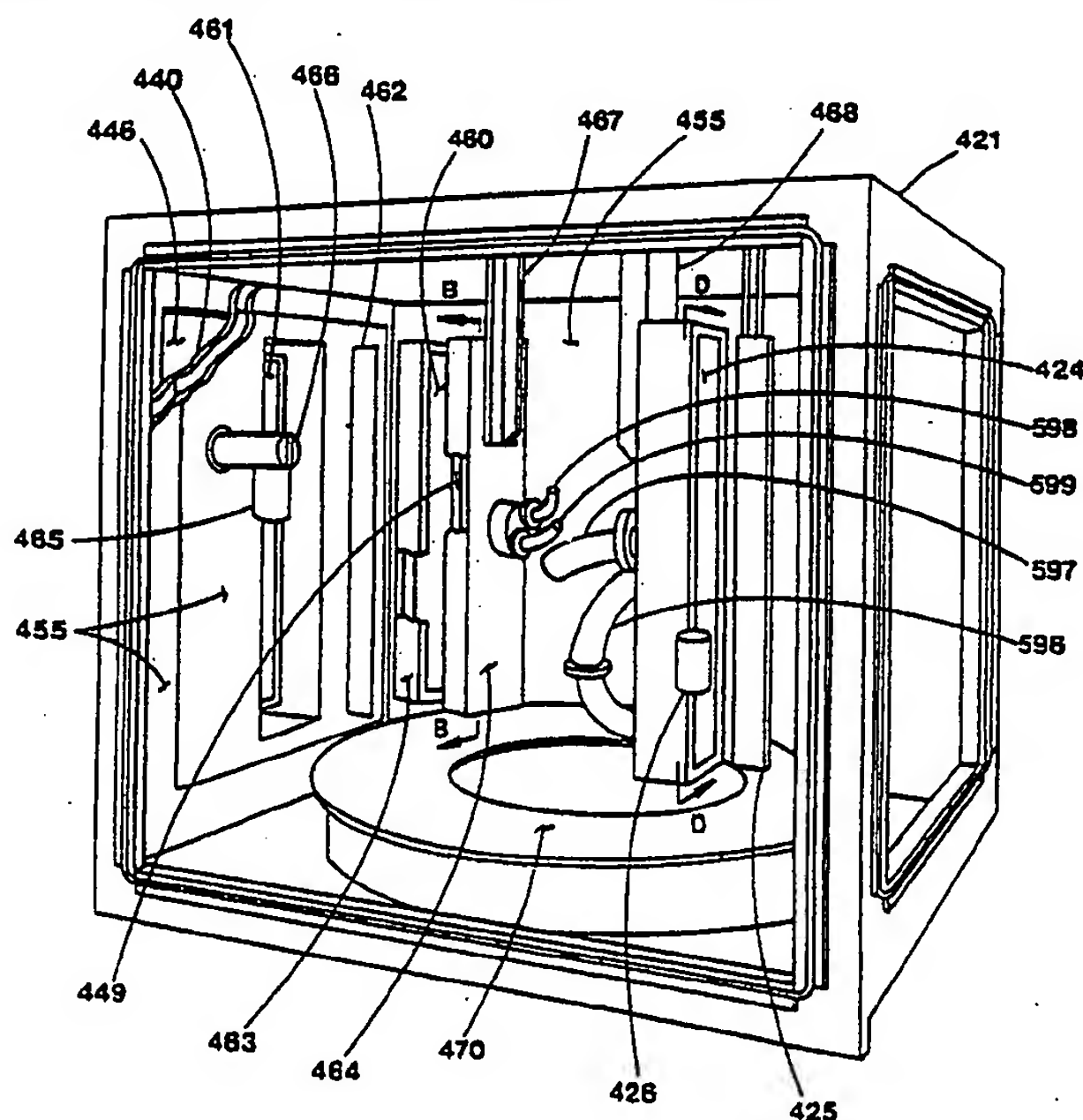
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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: PHYSICAL VAPOR DEPOSITION DUAL COATING APPARATUS AND PROCESS



(57) Abstract

A machine for covering a substrate (Fig. 14, 540) by means of both cathodic arc plasma deposition (CAPD) (Fig. 2) and magnetron sputtering (Fig. 1) without breaking vacuum in a single chamber (Fig. 14, 421). A computer system monitors (Fig. 3, 403, 405) and controls all coating process parameters to coat in any sequence multiple thin film layers using either the CAPD or magnetron sputtering process. A rotating substrate table (Fig. 14, 470) used in conjunction with internal and external targets coats both sides of the substrate simultaneously.

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PHYSICAL VAPOR DEPOSITION DUAL COATING  
APPARATUS AND PROCESS

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FIELD OF THE INVENTION

10 The present invention relates to vacuum coating  
production system utilizing both cathodic arc emission  
and magnetron sputtering processes.

BACKGROUND OF THE INVENTION

Sputtering Processes.

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Over the past 30 years or so there have been  
numerous reviews of sputtering and sputtering processes  
for film deposition.

20

Because there are so many interactions among  
parameters in sputtering systems, it is impossible to  
separate them completely.

25

Typically, the target (a plate of the material  
to be deposited or the material from which a film is to  
be synthesized) is connected to a negative DC voltage  
supply (or an RF power supply). The substrate is the  
material to be coated and it faces the target. The  
substrate may be grounded, floating, biased, heated,  
cooled, or some combination of these. A gas is  
introduced to provide a medium in which a glow discharge  
can be initiated and maintained. Gas pressures ranging  
from a few millitorr to several tens of millitorr are  
used. The most common sputtering gas is argon.

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When the glow discharge is started, positive  
ions strike the target plate and remove mainly neutral  
target atoms by momentum transfer, and these condense on  
the substrate to form thin films. There are, in  
addition, other particles and radiation produced at the  
target, all of which may affect film properties  
(secondary electrons and ions, desorbed gases, x-rays,  
and photons). The electrons and negative ions are

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5 accelerated toward the substrate platform and bombard it  
and the growing film. In some instances, a bias  
potential (usually negative) is applied to the substrate  
holder, so that the growing film is subject to positive  
ion bombardment. This is known variously as bias  
sputtering or ion plating.

10 In some cases, gases or gas mixtures other than  
Ar are used. Usually this involves some sort of reactive  
sputtering process in which a compound is synthesized by  
sputtering a metal target (e.g., Ti) in a reactive gas  
15 (e.g., O<sub>2</sub> or Ar-O<sub>2</sub> mixtures) to form a compound of the  
metal and the reactive gas species (e.g., TiO<sub>2</sub>).

#### Emission of Neutral Particles-The Sputtering Yield.

20 The sputtering yield is defined as the number of  
atoms ejected from a target surface per incident ion. It  
is the most fundamental parameter of sputtering  
processes. Yet all of the surface interaction phenomena  
involved that contribute to the yield of a given surface  
are not completely understood. Despite this, an  
impressive body of literature exists showing the yield to  
25 be related to momentum transfer from energetic particles  
to target surface atoms.

It is estimated that 1% of the energy incident  
on a target surface goes into ejection of sputtered  
particles, 75% into heating of the target and the  
30 remainder is dissipated by secondary electrons that  
bombard and heat the substrates. An improved process  
called magnetron sputtering uses magnetic fields to  
conduct electrons away from the substrate surface thereby  
reducing the heat.

35 There are three basic effects that occur at a  
substrate during glow discharge sputtering: (1)  
condensation of energetic vapor, (2) heating, and (3)  
bombardment by a variety of energetic species. The sum

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5 of all of these effects must be carefully controlled,  
and, since they are all interdependent, this is sometimes  
difficult.

For a given target material both deposition rate  
and uniformity are influenced by system geometry, target  
voltage, sputtering gas, gas pressure, and power. All  
10 other things being equal, rates are linearly proportional  
to power and decrease with increasing target-substrate  
separation. The sputtering gas influences deposition  
rate in the same way as it affects sputtering yields. As  
the gas pressure is increased the discharge current  
15 increases (increasing rate), but return of material to  
the target by backscattering also increases (decreasing  
rate). This is further complicated in some cases by  
increased Penning ionization at higher pressures which  
increases the rate by self-sputtering. The sum of all of  
20 this leads to gas pressure or a small range of gas  
pressure at which the rate is a maximum, and this must be  
determined empirically for each application. The optimum  
pressure may be anywhere between a few mTorr and several  
tens of mTorr.

25 In general, for a given gas pressure there will  
be an optimum target-substrate separation to produce the  
best uniformity. For small targets (15-cm diameter) this  
separation is generally small (a few centimeters), while  
for larger targets, the optimum separation may be  
30 considerably larger (10-20 cm).

Unquestionably, the hallmark of the sputtering  
processes described is versatility, both in terms of  
materials that can be deposited and process parameters  
that can be adjusted to tailor the properties of thin  
35 films as desired. However, the sheer number of critical  
process parameters and their complex interrelationships  
can often make these processes difficult to control. In  
general, these processes are found to be most useful in  
applications requiring rather thin films (generally 1  
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5 micron because of relatively low deposition rates) and/or  
in cases where the desired material simply cannot be  
deposited stoichiometrically any other way.

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reprinted with permission from the publishers of Thin  
10 Film Processes, edited by John L. Vossen and Werner Kern  
(copyright Academic Press, Inc., New York, 1978,  
pp. 12-62).

#### Cathodic Arc Plasma Deposition.

15 In the past ten years major advancements have  
been made in a related physical deposition process called  
cathodic arc plasma deposition (CAPD).

In the CAPD process target material is  
evaporated by the action of vacuum arcs. The target  
source material is the cathode in the arc circuit. The  
20 basic components of a CAPD system consist of a vacuum  
chamber, a cathode and an arc power supply, a means of  
igniting an arc on the cathode surface, an anode, a  
substrate and a substrate bias power supply. Arcs are  
sustained by voltages typically in the range of  
25 15 - 50 V, depending on the target cathodic material  
employed. Typical arc currents in the range of  
30 - 400 A are employed. Arcing is initiated by the  
application of a high voltage pulse to an electrode  
placed near the cathode (gas discharge ignition) and/or  
30 by mechanical ignition. The evaporation occurs as a  
result of the cathodic arc spots which move randomly on  
the surface of the cathode at speeds typically of the  
order of  $10^2$  m/s. The arc spot motion can also be  
controlled with the help of appropriate confinement  
35 boundaries and/or magnetic fields. The arc spots are  
sustained owing to material plasma generated with the arc  
itself. The target cathodic material can be a metal, a  
semiconductor or an insulator.

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5 The CAPD process is a unique process and is  
markedly different from other physical vapor deposition  
(PVD) processes. Some of the characteristic features of  
the CAPD process are as follows.

- (i) The core of the CAPD process is the arc  
spot which generates material plasma.
- 10 (ii) A high percentage (30% - 100%) of the  
material evaporated from the cathode surface is ionized.
- (iii) The ions exist in multiple charge states in  
the plasma, e.g. Ti,  $Ti^+$ ,  $Ti^{+2}$  and  $Ti^{+3}$  etc.
- (iv) The kinetic energies of the ions are  
15 typically in the range 10-100 eV.

These features result in deposits that are of  
superior quality compared with those from other physical  
vapor deposition processes. Some of these advantages are  
as follows.

- 20 (a) Good quality films over a wide range of  
deposition conditions, e.g. stoichiometric compound films  
with superior adhesion and high density, can be obtained  
over a wide range of reactive gas pressure and  
metal/refractory evaporation rates.
- 25 (b) High deposition rates for metals, alloys  
and compounds with excellent coating uniformity.
- (c) Low substrate temperatures.
- (d) Retention of alloy composition from source  
to deposits.
- 30 (e) Ease in deposition of compound films.

#### Cathodic Arc Emission Characteristics.

The cathodic arc results in a plasma discharge  
within the material vapor released from the cathode  
35 surface. The arc spot is typically a few micrometers in  
size and carries current densities as high as 10 amps per  
square micrometer. This high current density causes  
flash evaporation of the source material and the  
resulting evaporant consists of electrons, ions, neutral

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5 vapor atoms and microdroplets. The electrons are  
accelerated toward the cloud of positive ions. The  
emissions from the cathode spots are relatively constant  
over a wide range of arc current as the cathode spots  
split into a number of spots. The average current  
10 carried per spot depends on the nature of the cathode  
material.

It is likely that almost 100% of the material  
may be ionized within the cathode spot region. These  
ions are ejected in a direction almost perpendicular to  
the cathode surface. The microdroplets, however, have  
15 been postulated to leave the cathode surface at angles up  
to about 30° above the cathode plane. The microdroplet  
emission is a result of extreme temperatures and forces  
that are present within emission craters.

The cathodic arc plasma deposition process was  
20 considered unsuitable for decorative applications until  
recently, due to the presence of microdroplets in the  
film.

Latest developments involving elimination of  
microdroplets in the CAPD process has provided a  
25 significant alternative to existing techniques for a wide  
range of decorative applications. The CAPD process  
offers additional flexibility in the following areas:

(i) The controls of deposition parameters is  
less stringent than magnetron sputtering or ion plating  
30 processes.

(ii) The deposition temperature for compound  
films can be adjusted to much lower temperatures thus  
allowing the ability to coat substrates such as zinc  
castings, brass and even plastics without melting the  
35 substrate.

In summary the CAPD process offers many  
advantages over the traditional sputtering process noted  
above. However, certain decorative applications  
requiring a thin film are best accomplished with a  
40

5 sputtering process. One such application is applying a thin coating of gold on jewelry.

10 This is due to the difficulty of eliminating microdroplets in gold, copper, and silver coatings in CAPD processes. Therefore, sputtering is the preferred method today for depositing a thin gold coating for decorative purposes.

15 Gold, however, is relatively soft. Under conditions of continuous use it develops a diffusely reflecting appearance and is simultaneously worn away. See U.S. patent number 4,591,418 (1986) to Snyder. A coating of titanium nitride (TiN) using the improved CAPD process as disclosed in U.S. patent application serial number 07/025, 207 to Randhawa, incorporated herein by reference, creates excellent color matching to gold. Thus, it is possible to deposit titanium nitride on an inexpensive jewelry piece with Randhawa's improved CAPD process and then deposit real gold over the titanium nitride. Jewelry with this unique two layer coating offers the user a real gold plated piece plus a piece with the extremely wear resistant titanium nitride undercoat. Thus, if the real gold layer partially wears away, then the color matched titanium nitride retains the look of real gold in the worn away portion of the piece.

25 A difficulty in sequential layers of gold and TiN is that gold and TiN adhere very poorly to one another. Until the present invention, it is believed that only two basic methods were known to create multiple gold and TiN coatings. The first method is taught by Snyder, supra, which uses at least four interleaved layers of gold and TiN. The second method is taught by U.S. patent number 4,415,421 (1983) to Sasanuma. Sasanuma teaches simultaneous sputtering by means of an electron beam three different layers. Sasanuma attempts to overcome the poor adhesion between gold and TiN by

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5 including an intermediary layer of TiN and gold between  
the bottom layer of TiN and the top layer of gold.

The present invention overcomes these  
difficulties and provides a convenient single system to  
enable the direct coating of gold over TiN without  
adhesion problems. The present invention includes an  
10 advanced CAPD process and a modern magnetron sputtering  
process in a single machine.

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SUMMARY OF THE INVENTION

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It is, therefore, the object of the present invention to provide a machine capable of sequentially producing a coating using the CAPD process and the magnetron sputtering process.

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Another object of the present invention is to provide the machine with a computer controlled sequencing system.

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Another object of the present invention is to provide the machine with a common substrate turntable for both processes.

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Another object of the present invention is to provide the machine with the capability to coat both sides of a workpiece simultaneously with one process and then the other process.

Another object of the present invention is to provide the machine with a computer controlled reactant gas subsystem which can mix various gases with either process.

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Another object of the present invention is to provide the machine with a variable substrate bias voltage for enhanced process control.

Another object of the present invention is to provide the machine with a common vacuum pumping system for both processes.

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Another object of the present invention is to provide the machine with a common cooling system for both processes.

35

Another object of the present invention is to provide a system which allows pure gold to firmly adhere to a coating of a nitride or a carbonitride.

Another object of the present invention is to provide a system which allows pure gold to firmly adhere to a nitride or a carbonitride or a suitably hardened substrate.

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5 Another object of the present invention is to  
provide a system which can simultaneously coat a  
substrate using a CAPD process and a magnetron sputtering  
process.

10 Other objects of this invention will appear from  
the following description and appended claims, reference  
being made to the accompanying drawings forming a part of  
this specification wherein like reference characters  
designate corresponding parts in the several views.

Certain terms used herein are defined below:

15 Crossover setpoint: A defined pressure in the vacuum  
chamber where rough pumping ceases and diffusion  
pump and cold trap pumping take over to reduce  
pressure to high vacuum.

Hi-vac: A short-hand expression for high vacuum.

MilliTorr: One thousandth of a Torr. See below.

20 Substrate: Refers to the objects being coated.

Torr: A unit of pressure; that pressure necessary to  
support a column of mercury one millimeter high  
at zero degrees Celsius and standard gravity.

25 Plasma: A collection of charged particles containing  
equal numbers of positive ions and electrons and  
which is a good conductor of electricity and is  
affected by a magnetic field.)

The basic magnetron sputtering process is  
disclosed in Thin Film Processes, supra. Improvements  
30 are disclosed in U.S. patent numbers 4,162,954 (1979) and  
4,180,450 (1979) to Morrison, Jr. and assigned to the  
assignee of the present invention, Vac-Tec Systems, Inc.  
All these references are hereby incorporated herein by  
reference.

35 The basic CAPD process has evolved over the past  
twenty years. U.S. patent numbers 3,625,848 (1971) and  
3,836,451 (1974) to Snaper and assigned to Vac-Tec  
Systems, Inc. provide the origins of the basic process.  
U.S. patent number 4,430,184 (1984) to Mularie and  
40

5 4,724,058 (1988) to Morrison, Jr. both assigned to Vac-  
Tec Systems, Inc. provide improvements to the basic CAPD  
process. A summary of the CAPD art is provided in  
"Technical Note: A Review of Cathodic Arc Plasma  
Deposition Processes And Their Applications" by H.  
Randhawa and P.C. Johnson (Surface and Coatings  
10 Technology, 31 (1987 pp. 303-318). Further improvements  
to CAPD processing are disclosed in U.S. patent  
application serial number 07/025,207 to Randhawa and  
assigned to Vac-Tec Systems, Inc. All the above  
references are hereby incorporated by reference herein.

15 The present invention is a production CAPD and  
sputter coating system designed to deposit high  
performance metallurgical coatings onto a wide variety of  
substrates. It employs CAPD targets and sputter targets  
to deposit thin films of material onto substrates in a  
20 vacuum environment.

The sputter deposition process, using cathodes,  
is a relatively high voltage, low amperage process  
adaptable to depositing virtually any material. The  
process bombards the target material with positive ions,  
25 dislodging mainly neutral target atoms by momentum  
transfer. The dislodged atoms condense into thin films  
on the substrates.

The CAPD process uses a relatively high amperage  
and low voltage to evaporate an electrically conductive  
30 target source material and condense it onto the  
substrates to form a coating.

The preferred embodiment of the present  
invention employs two 5 x 24 inch (12.7 x 60.96 cm) CAPD  
targets and two 3.5 x 25 inch (8.89 x 93.5 cm) sputter  
35 targets to generate materials to be deposited.

A substrate fixture bearing the substrates  
rotates in the chamber. Alternatively the substrate may  
be variably passed in front of the targets by means of  
planetary motion, oscillation, or reciprocation. A  
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5 potentiometer or variable controller varies the speed of rotation according to the requirements of the deposition process.

10 DC bias power can be applied to the substrate fixture and substrates, during the deposition process, to enhance the movement of the target atoms toward the substrates and/or to effect the characteristics of the depositing film.

15 A diffusion pump, polycold trap (Meissner Trap), a cryogenic pump, or a turbomolecular pump create and maintain high vacuum in the chamber during the process. A mechanical pump evacuates the chamber to low vacuum (rough vacuum) and pumps (draws the exhaust away from) the diffusion pump or turbomolecular pump during high vacuum pumping.

20 A programmable logic controller (PLC) manages the process sequences. The system responds to the feedback of relevant processing parameters. Manual override is always available.

The major components of the present invention are:

- 25 1. the system main frame which supports and surrounds
- the processing chamber,
  - the diffusion pump and polycold trap,
  - water and compressed air distribution panels,
  - mass flow controllers and valves for process gasses,
  - monitoring instruments, and
  - electrical terminal board.
- 30 2. the system control console containing the control instruments,
- 35 3. two CAPD target power supplies,
4. the mechanical pump,
- 40 5. the compressor for the polycold trap,



- 5           6.    a power supply cabinet containing the  
              power supplies for the targets and bias,
7.    the power distribution cabinet and  
              transformer,
8.    the programmable logic controller (PLC)
9.    computer,
- 10          10.   the software for the computer, and
11.   the software for the PLC.

#### A Typical CAPD Process Cycle.

15           The operator loads the fixture with substrates  
and closes the front chamber door, sealing the chamber.  
The mechanical pump reduces pressure in the chamber to  
the crossover setpoint, typically set between 80 and 150  
milliTorr.

20           The chamber roughing valve closes when the  
chamber reaches the crossover setpoint; the hi-vac valve  
opens a few seconds later. The closing of the chamber  
roughing valve isolates the mechanical pump from the  
chamber; the opening of the hi-vac exposes the chamber to  
the diffusion pump and polycold trap.

25           The pump-down cycle ends when the diffusion pump  
reduces pressure in the chamber to a preset level,  
referred to as the base pressure and typically  $2 \times 10^{-5}$   
Torr. The drive motor then begins to rotate the  
substrate fixture.

30           The reduction of pressure to  $2 \times 10^{-5}$  Torr  
removes from the chamber most of the gas and water  
molecules which would otherwise interfere with the  
process.

35           Typically, nitrogen flows into the chamber,  
raising the pressure to  $1 \times 10^{-3}$  Torr or higher. The  
CAPD arc is then initiated. A high bias current  
initiates the cleaning cycle to clean the substrates with  
the sputtering action of ionized particles.

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5           The high bias cycle ends and the deposition  
cycle begins. Nitrogen gas back fills the chamber to  
operating pressure--a pressure between 5 and  $20 \times 10^{-3}$   
Torr.

10           Typically, nitrogen molecules combine with  
molecules of the CAPD target (i.e. titanium) during the  
reactive deposition process to form a coating of titanium  
nitride on the substrates; thus, the process consumes a  
portion of the nitrogen introduced into the chamber.

15           Nitrogen flows continuously into the chamber  
during the deposition process, requiring constant pumping  
by the high vacuum pump. The system balances the flow  
rate of the nitrogen with the pumping rate to keep  
pressure in the chamber at its operating pressure  
setpoint.

20           The system adjusts the flow rate of nitrogen  
with a mass flow controller, which compensates for the  
effect of pressure on the density of nitrogen and  
delivers standard volumes of gas regardless of pressure.

25           A negative voltage at the substrate accelerates  
the positively-charged ions of titanium en route from the  
targets. The negative voltage is called the bias voltage  
and is typically in the range of -50 to -500 volts of  
direct current (VDC).

30           The titanium targets are consumed during the  
deposition process and must be replaced periodically.

35           CAPD targets are connected to the negative  
output of the arc power supplies. Current flows from the  
arc targets through a plasma to an anode. Positively  
ionized particles of titanium, stripped from the target  
by the current, flow toward the negatively charged  
substrate, combining with nitrogen on the surface of the  
substrate to form the coating.

40           The PLC shuts off the nitrogen and power to the  
CAPD target sources at the conclusion of the deposition

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5 process and vents the chamber with nitrogen. When the  
chamber reaches atmospheric pressure, the PLC activates  
an audible signal.

Sputtering.

10 Sputtering is a relatively high voltage, low  
amperage, deposition process in contrast with a CAPD  
deposition process which employs relatively high  
amperages and low voltages.

15 Positive ions, generated in the glow discharge  
of the plasma, strike the target on the cathode and  
dislodge mainly neutral target atoms by momentum  
transfer.

The bombardment causes the target material to  
vaporize. Atoms dislodged from the targets condense into  
thin films on the substrate.

20 The targets in the preferred embodiment measure  
3.5 by 25 inches and are cooled by water.

Magnetron cathodes trap the plasma in a process  
chamber close to the target material by crossing  
electrical and magnetic fields. The eroding action of  
25 the plasma on the targets yields a high sputtering rate  
per watt of power.

The preferred embodiment of the present  
invention uses water cooled cathodes.

30 The operator may select from the following  
parameters from the PLC for a sputtering deposition  
cycle:

35 Sputter process time,  
Cathode #1 power setpoint,  
Cathode #2 power setpoint, and  
Sputter gas pressure

The operator selects the gas from the system  
control panel. Argon is the preferred gas for the  
sputtering deposition process because of its mass.

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5       The sputtering deposition cycle may also be  
automated. If the chamber is at base pressure, then the  
operator initiates the automated process by:

1.     Switching to SPUTTER from CAPD at the  
        deposition select panel.
2.     Entering the sputter parameters at the PLC.
- 10    3.     Pressing process START on the system  
        control panel.
4.     Adding bias power if desired.

15       The completion of the above noted CAPD and  
sputter process in the present invention will produce  
brilliant gold plated jewelry or a variety of other  
coatings on any substrate.

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BRIEF DESCRIPTION OF THE DRAWINGS

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- Fig. 1 Shows a schematic of a basic Planar Magnetron Sputtering System.
- Fig. 2 Shows a schematic of a basic Cathodic Arc Plasma Deposition (CAPD) System.
- 10 Fig. 3 Shows a schematic of the major components of the Dual Coating System of the invention.
- Fig. 4 Shows a right side elevational view of the Dual Coating System mainframe having
- 15 partial cutaways.
- Fig. 5 Shows a left side elevational view of the Dual Coating System mainframe having partial cutaways.
- Fig. 6 Shows the interior view of the right
- 20 chamber door of the Dual Coating System mainframe.
- Fig. 7 Shows the interior view of the left chamber door of the Dual Coating System mainframe.
- Fig. 8 Shows a front elevational view of the Dual
- 25 Coating System mainframe with the front chamber door and front enclosure panels cutaway.
- Fig. 9 Shows a top perspective view of the back of the Dual Coating System mainframe having
- 30 cutaways of all enclosure panels and the upper support frame.
- Fig. 10 Shows a top view of the mainframe of the Dual Coating System having all pumps removed.
- 35 Fig. 11 Shows a front elevational view of the left vacuum chamber door of the Dual Coating System mainframe having the enclosure panels removed.

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- 5            Fig. 12      Shows a front elevational view of the  
                 master control panel.
- Fig. 13      Shows a front perspective view of the  
                 vacuum chamber portion of the Dual Coating  
                 System mainframe. The front and right side  
                 doors are removed.
- 10           Fig. 14      Shows a front perspective view of the  
                 vacuum chamber and substrate fixturing.
- Fig. 15      Shows a top view cross section of the  
                 vacuum chamber showing all major process  
                 cathodes.
- 15           Fig. 16      Shows a longitudinal sectional view of the  
                 internally mounted sputtering cathode taken  
                 along line A-A of Fig. 15 which is  
                 coincident with the line B-B of Fig. 13.
- Fig. 17      Shows a longitudinal sectional view of the  
20                   internally mounted CAPD cathode taken along  
                 line C-C of Fig. 15 which is coincident  
                 with line D-D of Fig. 13.
- Fig. 18      Shows a front perspective view of a  
                 substrate clamp assembly for rings.
- 25           Fig. 19      Shows a software flow chart of the Program  
                 Logic Controller (PLC) logic.
- Fig. 20      Shows a continuation of Fig. 19.
- Fig. 21      Shows a software flow chart of the Personal  
                 computer (PC) logic.
- 30           Fig. 22      Shows a table of relative lusters and  
                 colors for various films produced by the  
                 present invention.

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DETAILED DESCRIPTION OF THE INVENTION

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Referring first to Fig. 1, a basic magnetron sputtering system comprises a vacuum chamber 1, a pump system 2, and a sputtering gas source 3. The vacuum chamber 1 houses a target/cathode 4 and an anode 5. Sputtering power supply 6 biases the target/cathode 4 negative and the anode 5 positive. The sputtering process uses a high voltage and low current power supply. A substrate 8 is a workpiece to be coated with a thin film 9. Substrate 8 is biased negative by substrate power supply 7.

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During the sputtering process the sputtering gas source 3 supplies non-reactant gas, argon. The pump system 2 maintains a vacuum in the range of a few milliTorrr to a few tens of milliTorrr. The sputtering power supply 6 powers up causing a glow discharge 10 between the anode 5 and the target/cathode 4.

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The glow discharge 10 causes positive ions of nonreactive gas, +, to bombard the target/cathode 4. See arrow 16. Momentum transfer causes neutral target atoms N, electrons e, and positive ions +, to dislodge from the target/cathode 4. Neutral target atoms N condense into thin film 9 on substrate 8. See arrow 14. Additionally a small percentage of positive ions + also condenses on the substrate. Positive ions + and electrons e also bombard the substrate 8 while thin film 9 is growing. See the arrows 12 and 13.

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A magnet 20 is located behind the target/cathode 4. The magnet 20 creates a magnetic field around the target/cathode 4 as shown by lines 22. The magnetic field 22 is typically in the order of a few hundred gauss. Magnetic field 22 traps a substantial number of electrons e against the target/cathode surface 23. This effect of trapping the electrons e serves two basic purposes. First fewer electrons reach the substrate 8,

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5 thereby maintaining the substrate 8 at a cooler  
temperature. Second the constant motion of the electrons  
e at target/cathode surface 23 enhances the sputtering  
yield, the emission rate of neutral particles N, from the  
target/cathode surface 23. This enhanced sputtering  
10 yield allows a faster growing of thin film 9 on the  
substrate 8. Thus a manufacturing efficiency is realized  
by reducing the time necessary to coat thin film 9 on  
substrate 8.

Referring next to Fig. 2 a basic cathodic arc  
plasma deposition (CAPD) system comprises a vacuum  
15 chamber 1, a pump 2, and an optional gas source 30. The  
vacuum chamber 1 houses a target/cathode 40 and an anode  
50. CAPD power supply 60 biases the target/cathode 40  
negative and the anode 50 positive. The CAPD process  
uses a low voltage and high current power supply. A  
20 substrate 8 is a workpiece to be coated with a thin film  
90. Substrate 8 is biased negative with respect to  
ground by substrate power supply 70.

During the CAPD process at least one gas 33 is  
introduced into the vacuum chamber 1 by gas source 30.  
25 The pump system 2 maintains a vacuum in the range of  $1 \times 10^{-4}$  Torr to  $1 \times 10^{-3}$  Torr. The substrate power supply  
70 biases the substrate 8 to a high voltage in the range  
of 200 to 1000 volts DC. RF voltages may be used for  
non-conducting materials.

30 Next the CAPD power supply 60 applies voltage to  
the target/cathode 40 and the anode 50. Next the arc  
starter 44 ignites an arc 100 between the target/cathode  
40 and the anode 50. An arc spot 29 forms on the  
target/cathode surface 230. The arc spot 29 moves at a  
35 speed of the order of a hundred meters per second on the  
target/cathode surface 230. Multiple arc spots 29 are  
created by using higher arc currents. The arc spot 29  
moves under the control of the magnet 200 in a  
predetermined pattern. The magnet 200 produces a

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5 magnetic field 220 in the range of 10-50 gauss. The arc  
spot(s) 29 is confined to the target/cathode surface 230  
by means of an insulating border 333.

10 The arc spot(s) vaporizes the target/cathode 40  
thus forming a stream of positive ions +, electrons e,  
droplets D, and neutral atoms n. The droplets D are  
removed from the stream by means of deposition shields  
555. Droplet removal shields 555 are suitably placed in  
front and to the sides of target/cathode 40.

15 The electrons e flow to the anode 50 of the arc  
circuit. The positive ions + bombard the substrate 8  
thereby cleaning and heating the substrate 8.

After adequate cleaning additional gas or gasses  
33 are added into the vacuum chamber 1 to establish  
pressures in the range of  $1 \times 10^{-3}$  Torr to  $5 \times 10^{-2}$  Torr.

20 Next the substrate 8 is biased by substrate  
power supply 70 to a lower voltage in the range of 50 -  
200 volts DC or RF.

25 Maintaining the arc 100 causes the thin film 90  
to grow on the substrate 8 by the deposition of positive  
ions + and a small percentage of neutral atoms n. The  
thin film 90 thickness and the rate of deposition are  
controlled by varying the arc current, vacuum chamber 1  
pressure, the substrate 8 bias voltage, the substrate  
temperature and the process time.

30 Referring next to Fig. 3 the Dual Coating System  
400 comprises a mainframe 401, a master control panel  
402, a programmable logic controller (PLC) 403, PLC  
software 404, a personal computer (PC) 405, PC software  
406, a power distribution panel 407, arc source power  
supplies 408, 852, a substrate bias power supply 409,  
35 sputtering power supplies 410, 575, a control unit for  
the cryogenic trap 411, and a mechanical pump 452.

Referring next to Fig. 4 the right side of the  
Dual Coating mainframe 401 has a support skeleton 412,  
leveling feed 413, enclosure panels 414, 415, 416, 417,

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5 418, 419, and 420, vacuum chamber 421, front chamber door  
422, right side chamber door 423, CAPD cathode 424, CAPD  
anode 425, arc starter 426, process gas mass flow control  
valves 427, a flow sensor 850, process gas supply pipe  
428, a compressed air supply pipe 429, a compressed air  
10 pressure regulator 430, a compressed air filter 431, a  
cooling water supply manifold 432, a cooling water flow  
control valve 434, a cooling water safety switch 435, and  
an electrical terminal board 436.

Multiple chamber doors 422, 423 serve to offer  
ease of access to internal components for maintenance as  
15 well as flexibility in loading and unloading workpieces.  
Compressed air components 429, 430, and 431 operate the  
pneumatic valves in the Dual Coating System 400. Cooling  
water components 432 and 434 distribute and control  
cooling water to the internal chamber pipes 437. Inlet  
20 port 438 and outlet port 439 in combination with internal  
chamber pipes 437 and cooling water supply manifold 432  
form an internal water cooled surface 400 around vacuum  
chamber 421. Cooling water safety switch 435 working in  
conjunction with master control panel 402 shuts off all  
25 power if cooling water flow drops below a predetermined  
setpoint. The electrical terminal board 436 serves as  
the common termination point for all wiring to the  
mainframe 401.

Referring next to Fig. 5 mainframe 401 has  
30 enclosure panels 441, 442, 443, 444, 445, 419 and 420,  
left side chamber door 446, cooling water filter 447,  
cooling water regulator 448, sputtering cathode 449,  
sputtering anode 464, and high vacuum pumping port 450.

Mainframe 401 has three chamber doors 446, 422  
35 and 423 for process and maintenance flexibility. High  
vacuum pumping port 450 connects to the cryogenic trap  
489 and the diffusion pump 451 (Fig. 9).

Referring next to Fig. 6 the right chamber door  
423 contains the same internal chamber pipes 437 as the  
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rest of the chamber. Flexible hoses 453 and 454 carry  
5 cooling water into the right chamber door 423.

A deposition shield 455 overlays the water cooled surface 440. Deposition shield 455 is generally made of stainless steel and serves to protect the underlying surfaces from the deposition processes.

10 A viewport 456 allows users to peer into the vacuum chamber 421. A viewport shutter 457 is manually placed in front of the viewport 456 to protect the viewport 457 from the deposition process.

Referring next to Fig. 7 the left chamber door  
15 446 has internal chamber pipes 437 and flexible hoses 458 and 459, and deposition shield 455. A door mounted sputtering cathode 460 is powered during the sputtering process. A door mounted CAPD cathode 461 is powered during the CAPD process. Sputtering anode 463 and CAPD  
20 anode 462 are shown. Arc starter 465 starts the vacuum arc during the CAPD process.

The substrate temperature monitor 466 is an infrared sensor.

Referring next to Figure 8 vacuum chamber 421  
25 houses internally mounted CAPD cathode 424 and the corresponding CAPD anode 425, the CAPD cathode mounting bracket 468 internally mounted sputtering cathode 449, and the corresponding sputtering anode 464, the sputtering cathode mounting bracket 467, door mounted  
30 sputtering cathode 460 and the corresponding sputtering anode 463, a second substrate temperature infrared sensor 469, the substrate turntable 470, and the substrate mounting fixture 471.

The substrate turntable 470 rotates under the  
35 control of the master control panel 402 during either the sputtering or CAPD process. The substrate mounting fixture 471 is custom designed for various substrates.

A substrate turntable drive assembly 472  
comprises a drive motor 473, a drive belt 474, a

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5     turntable drive shaft 475, a rotary vacuum seal 476,  
substrate bias voltage connection 477, and the substrate  
bias voltage cable 478.

Drive motor 473 is a variable speed unit  
enabling precise control of the substrate turntable 470  
speed. The rotary vacuum seal 476 maintains the  
10 integrity of the vacuum chamber 421 during processes.  
The bias voltage cable 478 connects to the substrate bias  
power supply 409 (Fig. 3).

Referring next to Figure 9 the Dual Coating  
System pumping assembly 479 is shown. The pumping  
15 assembly 479 starts with the mechanical pump 452.  
Mechanical pump 452 pumps the vacuum chamber to a  
crossover pressure ranging from 60 to 90 mTorr.  
Mechanical pump 452 connects to the vacuum chamber 421  
through the inlet pipe 480, the inlet filter 481, the  
20 connector pipe 482, the roughing valve 483 and the  
chamber roughing port 484.

Thermocouple gauge 485 measures vacuum chamber  
421 pressure and transmits this pressure to the master  
control panel 402 (Fig. 3). When the vacuum chamber 421  
25 pressure reaches a predetermined crossover pressure  
ranging from 60 to 90 mTorr, the master control panel 402  
closes the roughing valve 483 and opens the foreline valve  
485 and opens the high vacuum valve 487. These valve  
actions connect the mechanical pump 452 in series with  
30 the diffusion pump 451. These serial pumps 451 and 452  
are connected to the vacuum chamber 421 through the high  
vacuum piping 488 and the cryogenic trap 489 and the  
throttle valve 490 and the high vacuum valve 487 and the  
chamber high vacuum port 450 (Fig. 5).

35     After the above noted crossover procedures are  
accomplished, the mechanical pump 452 maintains the  
diffusion pump foreline 491 at low pressure while the  
diffusion pump 451 further reduces the vacuum chamber 421  
pressure to a system base pressure ranging from  $2 \times 10^{-5}$

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5 to  $5 \times 10^{-7}$  Torr. Simultaneously the cryogenic trap 489  
condenses water vapor and other condensable gasses  
thereby increasing the efficiency of the diffusion pump  
451.

10 Process pressures are controlled by the master  
control panel 402 operating the throttle valve 490 in  
response to signals from the capacitance manometer sensor  
492. The foregoing control loop is known as a downstream  
pressure control system. The infrared temperature sensor  
493 views the substrates 540 through viewport 469, (see  
Fig. 8) thereby providing the temperature control signal  
15 to the master control panel 402.

When processing is complete the vacuum chamber  
421 is raised back to atmospheric pressure by means of  
vent valve 494.

20 Referring next to Fig. 10 the top of the vacuum  
chamber 495 is seen supported by the support skeleton  
412. Water inlet 497 provides cooling water to the  
internal chamber pipes 437 as supplied by the cooling  
water supply manifold 432, see Fig. 4. Water outlet 499  
is then returned to the cooling water supply manifold  
25 432.

CAPD cathode utility plate 500 contains the  
electrical power leads 501 to the anode and 502 to the  
cathode of the CAPD cathode 424 and CAPD anode 425 as  
seen in Fig. 4. Anode cooling water inlet 503 feeds CAPD  
30 anode 425, and the anode cooling water outlet 504 returns  
to the cooling water supply manifold 432. Insulating  
enclosure 505 protects the CAPD cathode utility plate 500  
from anode electricity. Cooling water inlet 591 supplies  
cooling water from the cooling water supply manifold 432  
35 (Fig. 4) to the CAPD cathode 424. An outlet 592 returns  
the cooling water to the cooling water supply manifold  
432.

Sputtering cathode utility plate 506 contains  
the electrical power leads 507 to the anode and 508 to  
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5 the cathode of the sputtering anode 464 and sputtering  
cathode 449 as shown in Fig. 5. Insulating enclosure 590  
insulates the sputtering cathode utility plate 506 from  
electricity. Cooling water inlet 496 provides cooling  
water to the sputtering cathode 449 from the cooling  
10 water supply manifold 432. Cooling water return provides  
the return to cooling water supply manifold 432.

Electric power for the arc starter 426 is  
supplied by leads 509 and 510. Electric power for the  
CAPD cathode electromagnet 530 is supplied by cable 531.

15 Shield armature 512 (see Fig. 15) is activated  
by activating assembly 511. Activating assembly 511  
consists of a pneumatic cylinder 515 and crank arm 516.

Vacuum chamber 421 pressure is sensed and  
transmitted by pirani gauge 517, thermocouple gauge 518  
and ion gauge 519. Pirani type gauge 517 measures  
20 pressures ranging from atmospheric to 1 mTorr.  
Thermocouple gauge 485 measures pressures ranging from  
atmospheric to 1 mTorr. Ion gauge 519 measures pressures  
ranging from 1 mTorr - 0.0001 mTorr. Thermocouple gauge  
518 triggers the master control panel 401 for switching  
25 the ion gauge 519 on.

Referring next to Fig. 11 the vacuum chamber 421  
is seen supported by the support skeleton 412. The left  
vacuum chamber door 520 opens for loading and  
30 maintenance. An enclosure panel 521 is cut away. Water  
inlet 522 and water outlet 523 feed the internal chamber  
pipes 437 from the cooling water supply manifold 432.  
Water inlet 593 supplies cooling water from the cooling  
water supply manifold 432 to the door mounted CAPD  
cathode 461. Outlet 594 returns the cooling water  
35 through the cooling water supply manifold 432.

The door mounted CAPD cathode 461 is mounted  
inside CAPD door enclosure 524. Power to the door  
mounted CAPD cathode is supplied by lead 525. Power to  
the CAPD anode 462 is supplied by lead 526. Cooling  
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5 water inlet 527 supplies cooling water from the cooling  
water supply manifold 432 to the door mounted CAPD anode  
462 as shown in Fig. 7. Cooling water return 528  
supplies the return to cooling water supply manifold 432.

Electrical insulating enclosure 529 electrically  
isolates the door mounted CAPD anode 462. Electrical  
10 insulating enclosure 532 electrically isolates the door  
mounted CAPD cathode 461. CAPD electromagnet 530 (Fig.  
17) is powered by cable 533. Water inlet 534 supplies  
cooling water from the cooling water supply manifold 432  
to the door mounted sputtering cathode 460 (see Fig. 7).  
15 The water returns via water outlet 535. Lead 536 powers  
the door mounted sputtering cathode 461. Leads 537 and  
538 power the arc starter 465 (Fig. 7).

An infrared sensor 539 measures the substrate  
540 temperature as shown in Fig. 8. The infrared sensor  
539 consists of a lens assembly 541, a fiber optic cable  
542, and the infrared sensing unit 543. Infrared sensing  
unit 543 measures and transmits the substrate 540  
temperature to the master control panel 402. High  
intensity light source 544 calibrates lens assembly 541.  
25 Enclosure safety switches 560 prevent operation if an  
enclosure panel is ajar.

Referring next to Fig. 12 the master control  
panel 402 consists of a substrate temperature transmitter  
545 which indicates temperatures from the infrared  
30 sensors 493 and 543 by means of gauge 546.

Substrate temperature transmitter 545 switches  
between infrared sensing units 493 and 543 and  
subsequently transmits the substrate temperatures to the  
programmable logic controller (PLC) 403.

35 The vacuum chamber pressure monitoring panel 547  
consists of a thermocouple gauge indicator 548 which  
senses inputs from the thermocouple sensor 518 (Fig. 10).  
The ion gauge indicator 549 senses inputs from the ion  
tube 519 (Fig. 10). The pirani gauge indicator 550  
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senses inputs from the pirani gauge sensor 517.

5 Additionally the pirani gauge indicator 550 transmits signals to the valve control panel 551 which in turn controls the roughing valve 483, the high vacuum valve 487, and the vent valve 494. The valve control panel 551 also controls the diffusion pump foreline valve 486 and  
10 the throttle valve 490 (Fig. 9).

The system control panel 552 consists of a drive motor 473 speed indicator/controller 553. Additionally the system control panel 552 provides a manual/automatic mode of operation by means of selector switch 554.

15 Manual control switch 558 offers manual control of the process gas mass flow control valve 427 (Fig. 4). To initiate either the CAPD or sputtering process master start switch 556 must be switched "on". Process termination may be manually accomplished by switching the  
20 process stop switch 557 "off". A process status board 559 indicates the statuses of vacuum chamber 421 pressure range, cooling water safety switch 435 (Fig. 4), enclosure safety switch 560 (Fig. 11) status, drive motor 473 overtorque indicator (Fig. 8), and the overall  
25 process enable status indicator.

The process selection panel 561 provides selection of either the CAPD or sputtering process by means of selector switch 562.

The arc control panel 563 displays the  
30 respective CAPD voltages and amperages by means of indicators 564, 565, 566, and 567. The operator may manually select whether to use one or both of the CAPD cathodes 424/461 by means of selector switches 568 and 569. The CAPD arc power may be manually controlled by  
35 potentiometers 570 and 571.

Varying substrate 540 surface areas require varying bias power requirements. Substrate bias power control module 572 controls the bias power supply 409 and indicates bias voltage by means of indicator 851. The  
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5 internal sputtering cathode controls the internal  
sputtering power supply 410. The door mounted sputtering  
cathode power control module 574 controls the door  
mounted sputtering power supply 575 (Fig. 3). Power  
indicators 853 and 854 integral to the sputtering cathode  
control modules 573 and 574 indicate the electrical power  
10 levels of the respective sputtering cathodes.

The capacitance manometer sensor 492 (Fig. 9)  
transmits a signal to the capacitance manometer  
controller 576. The vacuum chamber 421 pressure is  
indicated by the indicator 577 integral to the  
15 capacitance manometer controller 576. Additionally the  
capacitance manometer controller 576 provides an input  
signal to the process gas controller 578.

The process gas controller 578 displays the  
process gas flow by means of indicator 579. Flow sensor  
20 850 (Fig. 4) supplies input to the indicator 579. The  
process gas controller 578 modulates process gas mass  
flow control valve 427 in response to signals from the  
capacitance manometer controller 576, thereby controlling  
vacuum chamber 421 pressure. The foregoing control loop  
25 constitutes an upstream pressure control system.

Support panel 581 houses the PLC input module  
582. PLC input module 582 is used to key enter variable  
data into the PLC 403. The PLC 403 contains PLC software  
404 which automatically can control all the CAPD and  
30 sputtering process functions for the Dual Coating System  
400.

Figures 13, 14 and 15 show the spatial  
relationships of the main operating components of the  
Dual Coating System 400. Fig. 13 shows the substrate  
35 turntable 470. The internally mounted CAPD cathode 424  
is supported above and in close proximity to the  
substrate turntable 470 by means of the CAPD cathode  
mounting bracket 468. The corresponding CAPD anode 425  
and arc starter 426 are commonly mounted to the same CAPD  
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5 cathode mounting bracket 468. Utility cable 596 and 597  
house cooling water pipes and electrical conductors  
serving the internally mounted CAPD cathode 424.

10 The internally mounted sputtering cathode 449  
and corresponding anode 464 are mounted on the sputtering  
cathode mounting bracket 467. Corresponding utility  
cables 598 and 599 house cooling water pipes and  
electrical conductors serving the internally mounted  
sputtering cathode 449.

15 The door mounted sputtering cathode 460 and its  
corresponding anode 463 faces the internally mounted  
sputtering cathode 449 such that simultaneous sputtering  
coating on both sides of the substrate 540 can be  
accomplished.

20 The door mounted CAPD cathode 461 coats the  
outside of the substrate 540 while the internally mounted  
CAPD cathode coats the inside of the substrate 540. The  
corresponding CAPD arc starter 465 and anode 462 are  
mounted on the same left chamber door 446. The substrate  
temperature monitor 466 protrudes beyond the deposition  
shield 455.

25 Fig. 14 shows a typical mounting arrangement for  
small substrates such as rings. The substrate turntable  
470 is in electrical contact with the substrate mounting  
fixture 471 which in turn is in electrical contact with  
the substrate 540.

30 Fig. 15 shows in dotted lines how the shield  
armature 512 moves the sputtering cathode shields 513 and  
514 away from the sputtering cathodes 449 and 460 during  
the sputter coating. The shield armature 512 shown in  
solid lines moves the sputtering cathode shields 513 and  
35 514 in front of the sputtering cathodes 449 and 460 to  
protect them from being coated during the CAPD process.

An alternate embodiment (not shown) uses RF  
sputtering cathodes either in addition to or in lieu of

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the magnetron sputtering cathodes 449 and 460.

5 Additionally RF substrate biasing (not shown) may be used.

A second alternate embodiment (not shown) uses diode sputtering either in addition to or in lieu of the magnetron sputtering cathodes 449 and 460.

10 The droplet removal shields 555 (see Fig. 2) serve to remove all droplets D from the stream of positive ions, electrons, and neutral atoms vaporizing from the door mounted CAPD cathode 461 and the internally mounted CAPD cathode 424.

15 Referring to Figure 2 the droplets D comprise molten metal particles which if allowed to land on the substrate 8 results in rough and low luster films. This is unacceptable for decorative applications. It has been experimentally determined that droplets D are emitted at  
20 angles  $\theta$  or less.  $\theta$  has been found to be 30 degrees or less when the CAPD target 615 (Fig. 17) has a minimal area of ten square inches. The distance 557 of the droplet removal shields 555 and the opening 556 are selected to prohibit the droplets D from reaching the  
25 substrate 8 (Fig. 2).

The main purpose of the present invention is to provide a film having a high luster and a consistent color controllable to match various gold colors. Fig. 22 shows a sampling of films produced by the present  
30 invention. Sequence Numbers 8 and 9 list the 10 carat and 24 carat gold characteristics used herein as a standard.  $L^*$  denotes the luster or brilliance of the film as measured per the CIE Lab color coordinates.  $a^*$  denotes a range of red to green contents in the film.  
35 Positive  $a^*$  values denote red contents and negative  $a^*$  values denotes green contents in the film.  $b^*$  denotes a range of yellow to blue contents in the film. The

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5 positive b\* values indicate a high yellow content in the film. Negative values would indicate a blue content in the film.

Sequence numbers 1 through 7 show specific film characteristics produced by the CAPD process used in the Dual Coating System 400. Referring to Fig. 19 Block 1006  
10 varies the ratios of two process gasses (Fig. 2, 33) which comprise acetylene as a source of carbon, and nitrogen. Suitably adjusting the ratios of carbon and nitrogen in the titanium and zirconium based films results in the excellent matching of luster and color  
15 film characteristics relative to gold as shown in Fig. 22. Thus in the typical Dual Coating System 400 operation a CAPD film is produced from the above noted Fig. 22 Sequence Numbers 1 through 7. Next a gold film may be applied using the sputtering process as shown in  
20 Fig. 1.

The preferred embodiment produces in sequence the above noted two films during a single vacuum cycle (Fig. 19 Block 1004). The adhesion of a second film  
25 consisting of gold on top of a CAPD deposited film taken from the selection in Fig. 22 Sequence Numbers 1 through 7 is commercially acceptable. A commercially acceptable adhesion is determined by using a Scotch Tape Pull test. This test results in no gold removal.

The ultimate purpose of the Dual Coating System  
30 400 is to provide a single system which enables the direct coating of gold over TiN or ZrN without adhesion problems. In practice the gold wears off the substrate 8 (Fig. 1) thus exposing the TiN or ZrN film underneath. It is critical in the practice of the present invention  
35 that the substrate 8 maintain the same appearance as the gold film wears off. Thus the relative values in Fig. 22 Sequence Numbers 1 through 7 in relation to Sequence Numbers 8 and 9 are critical to the successful practice of the present invention.  
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Fig. 16 shows the internally mounted sputtering cathode 449 and corresponding anode 464 as seen in Figures 5, 8, 13 and 15. Internally mounted sputtering cathode 449 is comprised of cathode body 600, sputtering target 601, and magnet 602. Clamp 603 fastens the target 601 to the cathode body 600 and completes their electrical continuity. Lead 508 powers the internally mounted sputtering cathode 449. Cooling water inlet 496 supplies water to the cooling water passage 604 thereby cooling the target 601. Outlet 498 returns the cooling water to the cooling water supply manifold 432 (Fig. 4). O-ring 605 provides a waterproof seal between the target 601 and cathode body 600.

Corresponding sputtering anode 464 comprises an anode body 605, a dark space shield 606 and a utility hub 607. The dark space shield 606 restricts the plasma discharge to the target 601. The dark space shield is affixed to the anode body 605 by means of screws 608. The sputtering anode 464 is insulated from the internally mounted sputtering cathode 449 by means of insulators 610, Teflon bolts 609, and insulating ring 611. O-rings 612 and 613 maintain a vacuum seal between utility conduits 598 and 599 and the vacuum chamber 421.

Fig. 17 shows the internally mounted CAPD cathode 424 as seen in Figures 4, 8, 13, and 15. Internally mounted CAPD cathode 424 is comprised of cathode body 614, CAPD target 615, target edge insulating strip 616, cathode body insulation 617, cathode shroud 618, and magnet 530. Cathode shroud 618 is insulated from the cathode body 614 by means of insulators 619, 620 and 621 and Teflon screws 622. Target edge insulating strip 616 is fastened to the CAPD target 615 by means of insulating fasteners 623. O-ring 624 provides a vacuum and water seal between the cathode body 614 and the CAPD target 615. Cooling water passage 625 is supplied with cooling water from inlet 591, thereby cooling the CAPD

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5 target 615. Outlet 592 returns the cooling water to the  
cooling water supply manifold 432. O-rings 626, 627,  
628, 629, 630 and 631 maintain a vacuum seal between the  
cathode body 614 and cathode shroud 618 and the utility  
cables 596, 597 and 632. Utility cables 596, 597 and 632  
10 connect to the cathode shroud 618 by means of connection  
hubs 633, 634 and 635.

Power to the electromagnet 530 is supplied by  
cable 531. Gasket 636 maintains a water tight seal  
between the electromagnet 530 and the cathode body 614.  
Power to the CAPD cathode 424 is supplied by lead 637 and  
15 638 via connectors 639 and 640. Insulating sleeves 641  
and 642 insulate connectors 639 and 640 from the cathode  
shroud 618.

Referring next to Fig. 18 the substrate  
turntable 470 has a mounting surface 702 which supports  
20 the substrate mounting fixture 471. The substrate  
mounting fixture 471 further comprises a base column 701,  
and a variable length rod 704. A substrate clamp 703 is  
affixed to the variable length rod 704. Substrate clamp  
703 has a flexible spring consistency. A triangular  
25 shape supports the substrate 540 in three spots. A ring,  
bracelet, earring or similar shaped substrate can be  
firmly secured with minimal contact against the substrate  
clamp 703.

Referring next to Fig. 3, the PLC 403 has the  
30 following basic hardware capabilities:

- Memory for storage of an operating system
- Memory for storage of a process program
- Logic module for process program execution
- Logic module for input/output control

35 The PLC software 404 has the following basic functional  
capabilities:

- An operating system for controlling the PLC  
hardware
- A process program ladder logic module

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Referring next to Fig. 19 block 1000 shows the  
5 PLC operating system starting up and checking hardware  
diagnostics to ensure a fully functional PLC exists  
before proceeding further.

Block 1001 shows the PLC reading all of the Dual  
Coating System 400 signal inputs including substrate  
10 temperature transmitter 545, cooling water safety switch  
435 status, enclosure panels 414, 415, 416, 417, 418, 419  
and 420 status, thermocouple sensor 518 measuring vacuum  
pressure, ion tube 519, pirani gauge sensor 517, valve  
control panel 551, drive motor 473 speed  
15 indicator/controller 553, manual/automatic selector  
switch 554, CAPD or sputtering process master start  
switch 556, selector switch 562, process termination  
switch 557, cooling water safety switch 435, enclosure  
safety switch 560, voltage and amperage indicators 564,  
20 565, 566, and 567, CAPD cathode selector switches 568 and  
569, substrate bias control module 572, internal  
sputtering power supply 410, door mounted sputtering  
cathode power control module 574, power indicators 853  
and 854, capacitance manometer sensor 492, and the  
25 process gas controller 578.

Block 1002 shows the PLC 403 receiving variable  
recipe data from either the PC 405 or PLC input module  
582.

Additionally the PLC 403 can send data to the PC  
30 405 or to the PLC input module 582.

Block 1003 checks for a safe system including  
cooling water safety switch 435 status, enclosure panels  
414, 415, 416, 417, 418, 419 and 420 all closed, and the  
thermocouple gauge indicator 548 which must show a vacuum  
35 exists before proceeding further. Therefore, the program  
logic first assures that the Dual Coating System 400 has  
adequate water flow and has all safety covers in place  
and has all doors and openings sealed thereby ensuring a  
secured vacuum chamber 421.

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5           Block 1004 shows the logic for the sequencing of  
the mechanical pump 452, diffusion pump 451 and the  
cryogenic trap 489.

          Block 1005 shows the logic for selecting whether  
to proceed with CAPD or sputtering by reading selector  
switch 562.

10           Block 1006 shows the logic for controlling the  
CAPD process gas by means of the process gas controller  
578 which controls the mass flow control valves 427, and  
variable input process parameters from Block 1002. The  
15           PLC logic generates an error signal for pressure  
deviating from set point, and adjusts the mass flow  
control valves 427 accordingly.

          Block 1007 shows the first process specific step  
for the CAPD process. This first step requires enabling  
the CAPD power supplies 408 and/or 852. Next the CAPD  
20           magnet 530 is enabled. Next the substrate bias power  
supply 409 is enabled. Next the substrate turntable 470  
is activated. Next the substrate bias power supply 409  
is controlled to the command voltage as received from  
Block 1002. Next the arc starter(s) 426, 465 ignite the  
25           arc(s).

          The user has inputted a substrate temperature  
parameter into Block 1002. Now in Block 1008 the  
substrate temperature is brought up to setpoint by means  
of varying the CAPD power supplies 408 and 852, and the  
30           substrate bias power supply 409.

          Blocks 1009, 1010, 1011, 1012 execute time  
versus power consumption and substrate temperature  
setpoint recipes which have been input into Block 1002.

          Block 1012 terminates the CAPD process after a  
35           predetermined amp hour setpoint as received from Block  
1002.

          Block 1013 dictates whether to proceed with a  
sputtering process as predetermined from Block 1002.

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5       Block 1014 proceeds to an orderly shutdown by  
allowing the internal chamber pipes 437 to cool the  
substrate 540 to a predetermined temperature as dictated  
by Block 1002.

10       Block 1015 executes either an atmospheric vent  
by opening vent valve 494, or by introducing process gas  
by means of process gas control valves 427.

The sputtering process is started in Block 1016  
by introducing process gases by means of the process gas  
controller 578.

15       Next Blocks 1017, 1018 move the sputtering  
cathode shields 513, 514 in front of the sputtering  
cathodes 464 and 463. Block 1017 proceeds to power the  
sputtering power supplies 410, 575 in order to sputter  
clean the sputtering target/cathodes 449 and 460. Time  
duration for sputter cleaning is dictated by Block 1002.

20       Next Block 1019 removes the sputtering cathode  
shields 513 and 514 away from the sputtering target  
cathodes 449 and 460. The substrate turntable 470 is  
activated.

25       Next Block 1020 sputters for a predetermined  
time and sputtering power supplies 410, 575 supply power  
output as determined by block 1002.

Sputtering terminates with Blocks 1014 and 1015.

30       Block 1100 shows the PC running executive  
software and receiving variable process recipes.  
Variable process recipes include all time, temperature,  
power, flow and pressure variables the user desires for  
his process. Block 1101 shows the CRT on the PC  
displaying the variable input recipes. An optional print  
output Block 1102 is shown. Alternatively the variable  
35       process recipes may be entered by means of the PLC input  
module 582.

40       Block 1103, shows the PC translating the  
variable input recipes from engineering units to PLC

5       format data. Block 1104 shows the PC 405 storing and  
retrieving the variable input recipes.

Block 1105 controls all PC/PLC communications.  
Block 1106 shows the PLC 403 receiving the variable input  
recipes. Additionally the PLC 403 can be commanded by  
the PC 405 to transmit measured process parameters for  
10       display and storage by the PC 405.

Variable process recipes can be input into Block  
1100 concurrently with the execution of measured process  
parameter displays and storage in Blocks 1101, 1102 and  
1104.

15       The best mode for practicing the above noted  
computer art utilizes a Texas Instruments Series 500 PLC  
Model 530 C-1102.. The PC used herein is an IBM (or  
compatible) using a Microsoft operating system, MS-DOS,  
and EGA/VGA graphics. EGA/VGA graphics allow sixteen  
20       color displays, primitives and text. Asynchronous serial  
communications between the PLC and the PC utilize Texas  
Instruments Task Codes and assembly language routines.

The PLC ladder logic software is written using  
the Texas Instruments Tisoft Ladder Editor. The PC  
25       executive software is written in the "C" language using  
the Microsoft C compiler.

The executive software for the PC is menu driven  
thereby allowing the screen to prompt the user into  
entering variable recipes in engineering units. On line  
30       "help" prompts are available to the user as an exit from  
all screens. The executive software accepts all data in  
engineering units and converts all data to PLC machine  
readable data using "C" language subroutines.

The CRT Block 1101, printer Block 1102 and disk  
35       Block 1104 can receive and display or print or store all  
variable input process parameters in real time.

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CLAIMS

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## I Claim:

1. An apparatus for coating a substrate,  
comprising:

- 10 (a) a vacuum chamber;  
(b) a pumping system for creating a vacuum  
inside the vacuum chamber;  
(c) a substrate;  
(d) a sputtering target/cathode with an  
erosion face;  
15 (e) magnetic means located adjacent to the  
sputtering target/cathode on the  
opposite side of said erosion face of  
the sputtering target/cathode;  
20 (f) a sputtering anode for generating a  
plasma discharge for the sputtering  
target/cathode;  
(g) a sputtering power supply for  
generating an electric circuit between  
said sputtering target/cathode and  
25 said anode for the sputtering  
target/cathode;  
(h) means for introducing and controlling  
a process gas in the vacuum chamber to  
cause a glow discharge between the  
30 sputtering target/cathode and the  
anode, thereby vaporizing the erosion  
face and depositing a sputtering  
coating on the substrate;  
(i) a CAPD target/cathode, including an  
35 erosion face;  
(j) a CAPD anode for the CAPD  
target/cathode;

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(k) a CAPD power supply for generating an electric circuit between said CAPD target/cathode and said CAPD anode;

10

(l) means for starting an arc between said CAPD target/cathode and CAPD anode to cause an arc spot on the erosion face, thereby vaporizing the CAPD target/cathode erosion face and depositing a CAPD coating on the substrate; and

15

(m) means for sequentially controlling the application of a plurality of thin film coatings on the substrate.

2. The apparatus for coating a substrate in claim one, further comprising:

20

(a) means for mounting the substrate inside the vacuum chamber;

(b) means for electrically biasing the substrate;

25

(c) means for measuring the substrate electrical bias;

(d) means for measuring the power of the sputtering power supply;

(e) means for controlling the process gas pressure;

30

(f) means for measuring the substrate temperature;

(g) means for controlling the substrate temperature;

(h) means for measuring the power of the CAPD power supply; and

35

(i) means for cooling the vacuum chamber and the sputtering target/cathode and the CAPD target/cathode.

3. The apparatus for coating a substrate in claim one, further comprising a turntable in said vacuum

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5 chamber, which turntable is in electrical continuity with the substrate; and an upright substrate support stand on said turntable.

10 4. The apparatus for coating a substrate in claim three, wherein said upright support stand further comprises a clamp having a spring which contacts the substrate.

5. The apparatus for coating a substrate in claim three, further comprising a substrate bias power supply; a rotary vacuum seal for the turntable; and interconnecting power connections.

15 6. The apparatus for coating a substrate in claim one, further comprising means for electrically biasing the substrate; and a substrate electrical bias indicator integral to the electrically biasing means.

20 7. The apparatus for coating a substrate in claim one, further comprising means for measuring the power of the sputtering power supply and a power indicator integral to the sputtering power supply.

25 8. The apparatus for coating a substrate in claim one, wherein the means for introducing and controlling a process gas includes a capacitance manometer, a mass flow controller, a mass flow gas control valve, and a throttle valve.

30 9. The apparatus for coating a substrate in claim eight, wherein the means for introducing and controlling the process gas further includes an upstream pressure control loop.

35 10. The apparatus for coating a substrate in claim eight, wherein the means for introducing and controlling the process gas further includes a downstream pressure control loop.

11. The apparatus for coating a substrate in claim one, further comprising an infrared sensor; and an indicator for measuring the substrate temperature.

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5           12. The apparatus for coating a substrate in  
claim five, further comprising means to vary the rate of  
using CAPD sputtering; means to vary the power of the  
substrate bias power supplies; and means to vary the  
speed of the turntable.

10           13. The apparatus for coating a substrate in  
claim eleven, further comprising means for measuring the  
power of the CAPD power supply; and a power indicator to  
the CAPD power supply.

15           14. The apparatus for coating a substrate in  
claim two, wherein the means for starting the arc between  
said CAPD target/cathode and CAPD anode further comprise  
an arc starter.

20           15. The apparatus for coating a substrate in  
claim one, further comprising interconnected cooling  
water pipes for cooling the vacuum chamber and the  
sputtering target/cathode and the CAPD target/cathode.

25           16. The apparatus for coating a substrate in  
claim fifteen, wherein the interconnected cooling water  
pipes include a network of cooling water pipes located  
adjacent to the surface of the vacuum chamber, the  
sputtering target/cathode and the CAPD target/cathode.

30           17. The apparatus for coating a substrate of  
claim one, wherein the vacuum chamber further comprises  
three doors, internal chamber cooling water pipes, a  
deposition shield, and a viewport.

35           18. The apparatus for coating a substrate in  
claim one, wherein the pumping system further comprises a  
mechanical pump, a diffusion pump and a cryogenic trap.

40           19. The apparatus for coating a substrate in  
claim one, further comprising a substrate with an array  
of workpieces having two or more sides.

45           20. The apparatus for coating a substrate in  
claim one, further comprising a second sputtering  
target/cathode and a second CAPD target/cathode, so that  
the substrate can be simultaneously coated on both sides

5 by either at least two sputtering target/cathodes or at least two CAPD target cathodes.

21. The apparatus for coating a substrate in claim one, wherein the sputtering target/cathode further comprises movable shields, thereby protecting the sputtering target/cathode from being coated while the CAPD target/cathode is operating.

22. The apparatus for coating a substrate in claim one, wherein the sputtering target/cathode further comprises a cathode body, the magnetic means, cooling water passages adjacent the sputtering target, and connecting means for the aforesaid items.

23. The apparatus for coating a substrate in claim twenty one, wherein the sputtering anode further comprises an anode body integral to the cathode body, and a dark space shield, thereby restricting the plasma discharge to the sputtering target/cathode.

24. The apparatus for coating a substrate in claim one, wherein the CAPD target/cathode further comprises a cathode body, a target edge insulating strip, a CAPD magnet behind the erosion face, cooling water passages adjacent the target, and connecting means for the aforesaid items.

25. The apparatus for coating a substrate in claim one, wherein the CAPD anode further comprises integral cooling water pipes.

26. The apparatus for coating a substrate in claim one, wherein the sputtering target/cathode erosion face is inside the vacuum chamber.

27. The apparatus for coating a substrate in claim one, wherein the CAPD target/cathode erosion face is inside the vacuum chamber.

28. The apparatus for coating a substrate in claim one, wherein the CAPD target/cathode further comprises means for removing droplets from the vaporizing CAPD target/cathode erosion face.

5           29. The apparatus for coating a substrate in  
claim twenty eight, wherein the means for removing  
droplets from the vaporizing CAPD target/cathode erosion  
face further comprises a droplet removal shield having a  
location in front of the CAPD target/cathode erosion  
10          face, thereby preventing droplets from reaching the  
substrate.

30. The apparatus for coating a substrate in  
claim one, wherein the CAPD coating has substantially the  
same luster and color of gold.

15          31. The apparatus for coating a substrate in  
claim one, wherein the CAPD coating is a metal selected  
from the group consisting of titanium, zirconium, carbon  
and nitrogen.

20          32. The apparatus for coating a substrate in  
claim one, wherein the sputtering coating and the CAPD  
coating are sequentially produced in the vacuum chamber  
without eliminating the vacuum.

25          33. The apparatus for coating a substrate of  
claim two, further comprising a computer system, wherein  
the computer system monitors and controls the pumping  
system, the process gas system, the means for  
electrically biasing the substrate, the means for  
controlling the substrate temperature, the means for  
cooling the vacuum chamber, and the sputtering and CAPD  
power supplies.

30          34. The apparatus for coating a substrate of  
claim thirty three, wherein the computer system further  
comprises a program logic computer (PLC) and a personal  
computer (PC) interconnected to the PLC.

35          35. The apparatus for coating a substrate of  
claim thirty four, wherein the PLC contains ladder logic  
software for monitoring and controlling the pumping  
system, the process gas system, the means for  
electrically biasing the substrate, the means for

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5 controlling the substrate temperature, the means for  
cooling the vacuum chamber, and the sputtering and CAPD  
power supplies.

10 36. The apparatus for coating a substrate of  
claim thirty five, wherein the PC further comprises  
executive software having menus for entering variable  
parameters into the PLC ladder logic software, and  
further comprising software to indicate the status of the  
PLC ladder logic software.

15 37. The apparatus for coating a substrate of  
claim thirty six, wherein the executive software further  
comprises screen prompted table inputs for entering  
variable parameters into the PLC ladder logic software.

20 38. The apparatus for coating a substrate of  
claim thirty six, wherein the executive software further  
comprises multicolor high resolution graphics.

25 39. A computer system, comprising:  
(a) a PLC;  
(b) a PC;  
(c) means for communicating data between  
the PLC and the PC;  
(d) means for inputting variable process  
parameters from a CAPD and sputtering  
dual coating system; said variable  
process parameters including pumping  
system data, process gas data,  
30 substrate biasing data, substrate  
temperature data, vacuum chamber  
cooling data, and CAPD and sputtering  
power supply data;  
(e) means for inputting variable process  
35 recipes from a user; and  
(f) means for sending control signals to  
the CAPD and sputtering dual coating  
system, thereby controlling the

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variable process parameters to the values of the variable process recipes.

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40. A method for depositing multiple thin film coatings on a substrate, comprising the steps of:

- (a) placing the substrate in a chamber;
- (b) evacuating the chamber;
- (c) activating a CAPD target/cathode in the chamber;
- (d) depositing a thin CAPD film on the substrate;
- (e) injecting a process gas into the chamber;
- (f) activating a magnetron sputtering target/cathode in the chamber;
- (g) creating a plasma discharge in the chamber; and
- (h) depositing a thin sputtering film on the substrate.

25

41. The method for depositing multiple thin film coatings on a substrate in claim forty, further comprising the steps of:

- (i) cooling the chamber;
- (j) controlling all the foregoing process steps by means of a computer system.

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42. The method for depositing multiple thin film coatings on a substrate in claim forty, further comprising the steps of:

- (k) shielding the CAPD droplets from the substrate.

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43. The method for depositing multiple thin film coatings on a substrate in claim forty, further comprising the steps of:

- (l) controlling the thin CAPD film to be substantially the same luster and color as gold.

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5 44. The method for depositing multiple thin  
film coatings on a substrate in claim forty, further  
comprising the steps of:

- (m) controlling the thin sputtering film  
to be firmly adhered to the thin CAPD  
film.

10 45. The method for depositing multiple thin  
film coatings on a substrate in claim forty, wherein the  
chamber vacuum is not broken between the CAPD deposition  
and the spotting deposition except by injecting of the  
process gas.

15 46. An apparatus for coating a substrate  
comprising:

- (a) a vacuum chamber;
- (b) gas process means for creating a  
vacuum and for introducing and  
20 controlling process gas within the  
vacuum chamber;
- (c) CAPD means in the vacuum chamber;
- (d) magnetron sputtering means in the  
vacuum chamber; and
- 25 (e) means for sequentially controlling the  
application of a plurality of thin  
films by said CAPD means and magnetron  
sputtering means.

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[received by the International Bureau on 2 October 1989 (02.10.89)  
original claims 1,2,12,14,19 and 45 amended;  
other claims unchanged (4 pages)]

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## I Claim:

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1. An apparatus for coating a substrate, comprising:
  - (a) a vacuum chamber;
  - (b) a pumping system for creating a vacuum inside the vacuum chamber;
  - (c) means for mounting the substrate inside the vacuum chamber;
  - (d) a sputtering target/cathode with an erosion face inside of said vacuum chamber;
  - (e) magnetic means located adjacent to the sputtering target/cathode on the opposite side of said erosion face of the sputtering target/cathode;
  - (f) a sputtering anode for generating a plasma discharge for the sputtering target/cathode;
  - (g) a sputtering power supply for generating an electric circuit between said sputtering target/cathode and said anode for the sputtering target/cathode;
  - (h) means for introducing and controlling a process gas in the vacuum chamber to cause a glow discharge between the sputtering target/cathode and the anode, thereby vaporizing the erosion face and depositing a sputtering coating on the substrate;
  - (i) a CAPD target/cathode, including an erosion face inside of said vacuum chamber;
  - (j) a CAPD anode for the CAPD target/cathode;

- 5 (k) a CAPD power supply for generating an electric circuit between said CAPD target/cathode and said CAPD anode;
- 10 (l) means for starting an arc between said CAPD target/cathode and CAPD anode to cause an arc spot on the erosion face, thereby vaporizing the CAPD target/cathode erosion face and depositing a CAPD coating on the substrate; and
- 15 (m) means for sequentially controlling the application of a plurality of thin film coatings on the substrate.

2. The apparatus for coating a substrate in claim one, further comprising:

- 20 (a) means for electrically biasing the substrate;
- (b) means for measuring the substrate electrical bias;
- (c) means for measuring the power of the sputtering power supply;
- 25 (d) means for controlling the process gas pressure;
- (e) means for measuring the substrate temperature;
- (f) means for controlling the substrate temperature;
- 30 (g) means for measuring the power of the CAPD power supply; and
- (h) means for cooling the vacuum chamber and the sputtering target/cathode and the CAPD target/cathode.
- 35

3. The apparatus for coating a substrate in claim one, further comprising a turntable in said vacuum

12. The apparatus for coating a substrate in  
5 claim five, further comprising means to vary the rate of  
CAPD and sputtering; means to vary the power of the  
substrate bias power supplies; and means to vary the  
speed of the turntable.

13. The apparatus for coating a substrate in  
10 claim eleven, further comprising means for measuring the  
power of the CAPD power supply; and a power indicator to  
the CAPD power supply.

14. The apparatus for coating a substrate in  
claim one, wherein the means for starting the arc between  
15 said CAPD target/cathode and CAPD anode further comprise  
an arc starter.

15. The apparatus for coating a substrate in  
claim one, further comprising interconnected cooling  
water pipes for cooling the vacuum chamber and the  
20 sputtering target/cathode and the CAPD target/cathode.

16. The apparatus for coating a substrate in  
claim fifteen, wherein the interconnected cooling water  
pipes include a network of cooling water pipes located  
adjacent to the surface of the vacuum chamber, the  
25 sputtering target/cathode and the CAPD target/cathode.

17. The apparatus for coating a substrate of  
claim one, wherein the vacuum chamber further comprises  
three doors, internal chamber cooling water pipes, a  
deposition shield, and a viewport.

18. The apparatus for coating a substrate in  
30 claim one, wherein the pumping system further comprises a  
mechanical pump, a diffusion pump and a cryogenic trap.

19. The apparatus for coating a substrate in  
claim one, further comprising a substrate holder for  
35 holding an array of workpieces having two or more sides.

20. The apparatus for coating a substrate in  
claim one, further comprising a second sputtering  
target/cathode and a second CAPD target/cathode, so that  
the substrate can be simultaneously coated on both sides

5 44. The method for depositing multiple thin film coatings on a substrate in claim forty, further comprising the steps of:

- (m) controlling the thin sputtering film to be firmly adhered to the thin CAPD film.

10 45. The method for depositing multiple thin film coatings on a substrate in claim forty, wherein the chamber vacuum is not broken between the CAPD deposition and the sputtering deposition except by injecting of the process gas.

15 46. An apparatus for coating a substrate comprising:

- (a) a vacuum chamber;
- (b) gas process means for creating a vacuum and for introducing and  
20 controlling process gas within the vacuum chamber;
- (c) CAPD means in the vacuum chamber;
- (d) magnetron sputtering means in the vacuum chamber; and
- 25 (e) means for sequentially controlling the application of a plurality of thin films by said CAPD means and magnetron sputtering means.

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## STATEMENT UNDER ARTICLE 19

Following receipt of the International Search Report, the accompanying Amendments of Claims is hereby submitted pursuant to Article 19 of the PCT. Pursuant to Article 19(1) this statement of explanation is respectfully submitted.

Claim 1: Claim 1 has been amended in order to more particularly point out and distinctly claim the subject matter of the invention. In particular, elements (d) and (i) are specifically related to the other elements claimed by clarifying that they are found inside of the vacuum chamber. Also, element (c) "a substrate" is replaced with the means for mounting the substrate inside the vacuum chamber.

Claim 2: The means for mounting the substrate were moved to the independent claim 1 and were therefore removed from dependent claim 2.

Claim 12: Claim 12 has been amended to correct a typographical error.

Claim 14: This claim may depend from independent claim 1 as well as from dependent claim 2.

Claim 19: Claim 19 has been amended in order to more particularly point out and distinctly claim the subject matter of the invention.

Claim 45: Claim 45 has been amended to correct a typographical error.

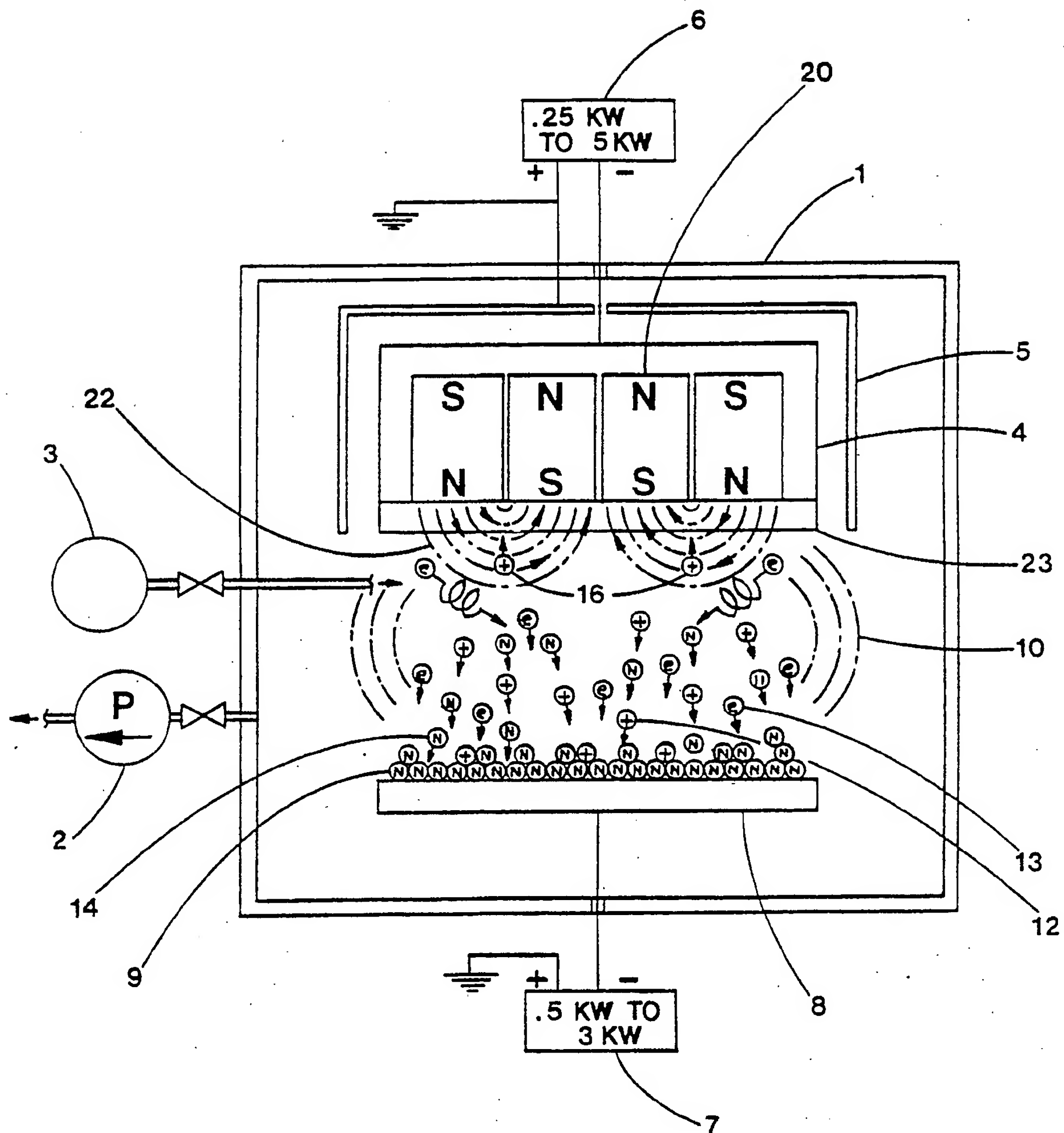


FIG. 1

SUBSTITUTE SHEET

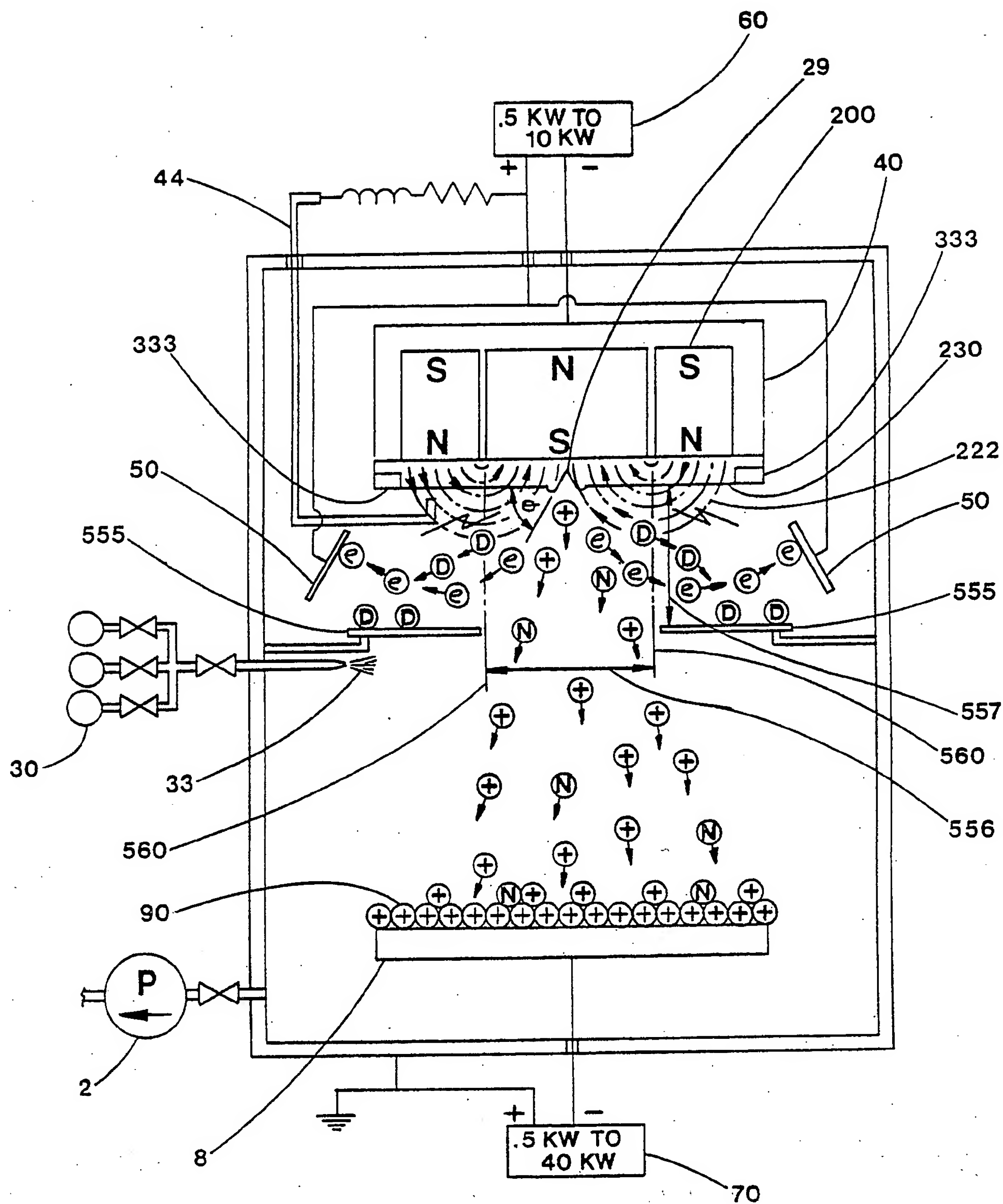
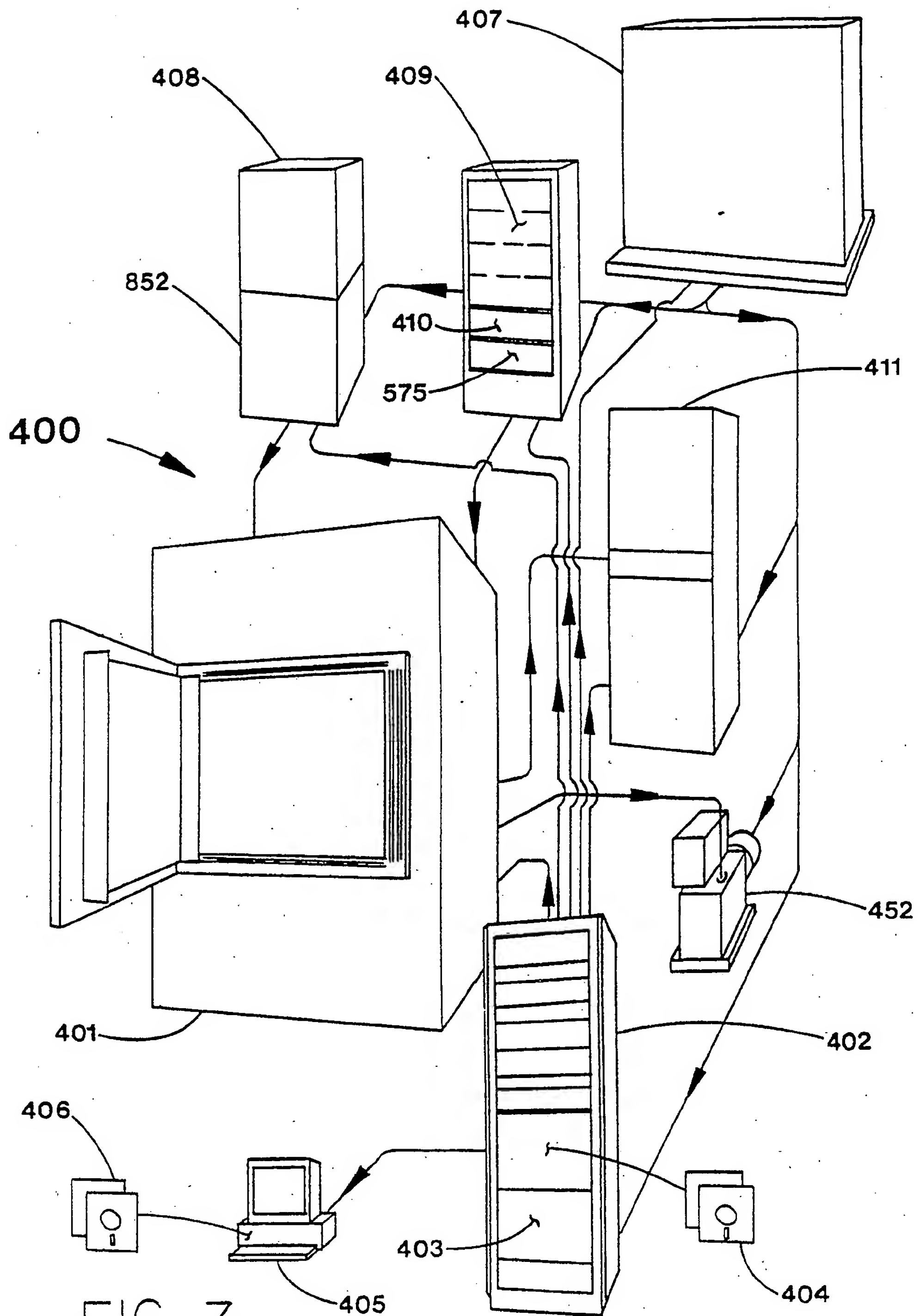
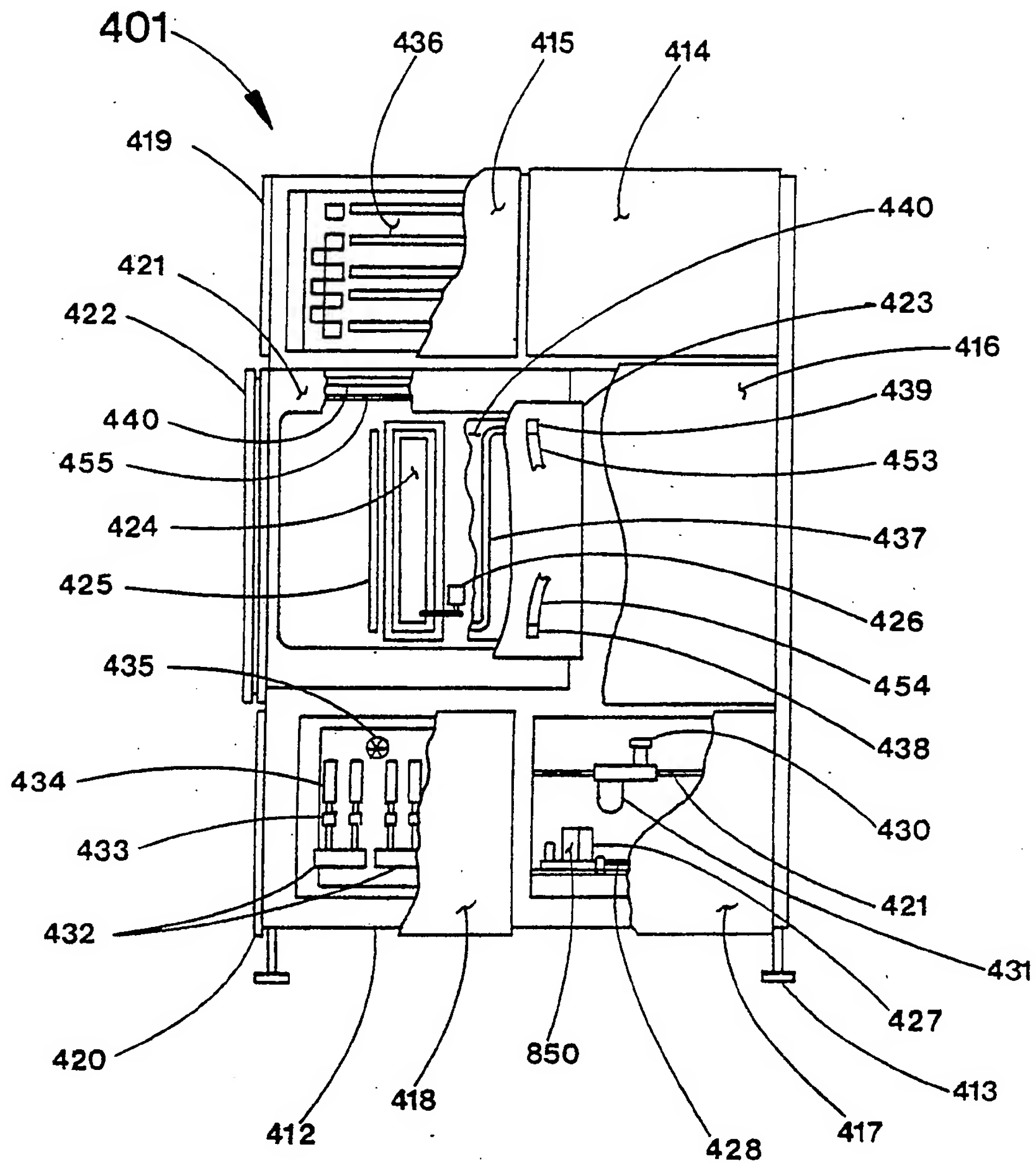


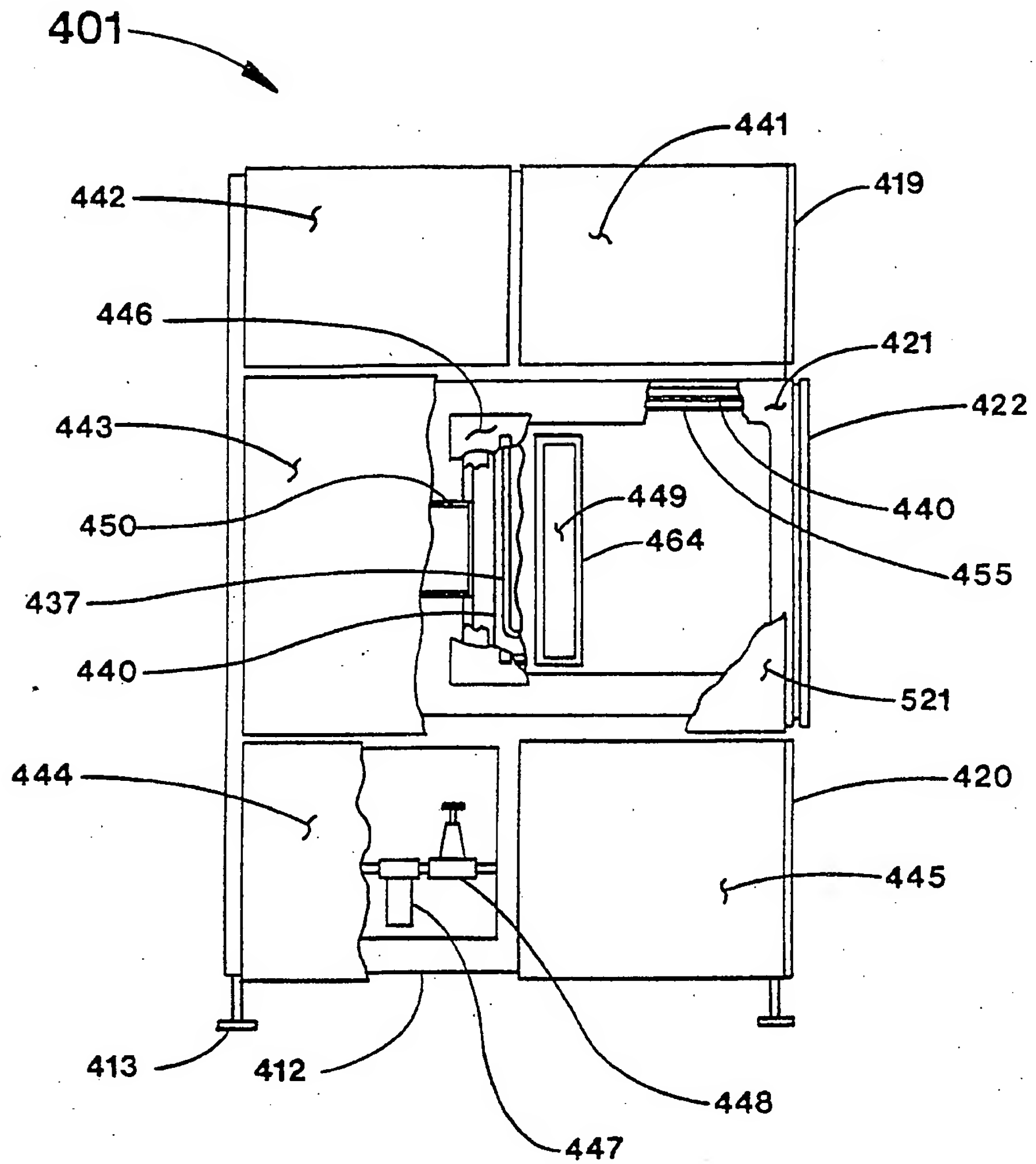
FIG. 2

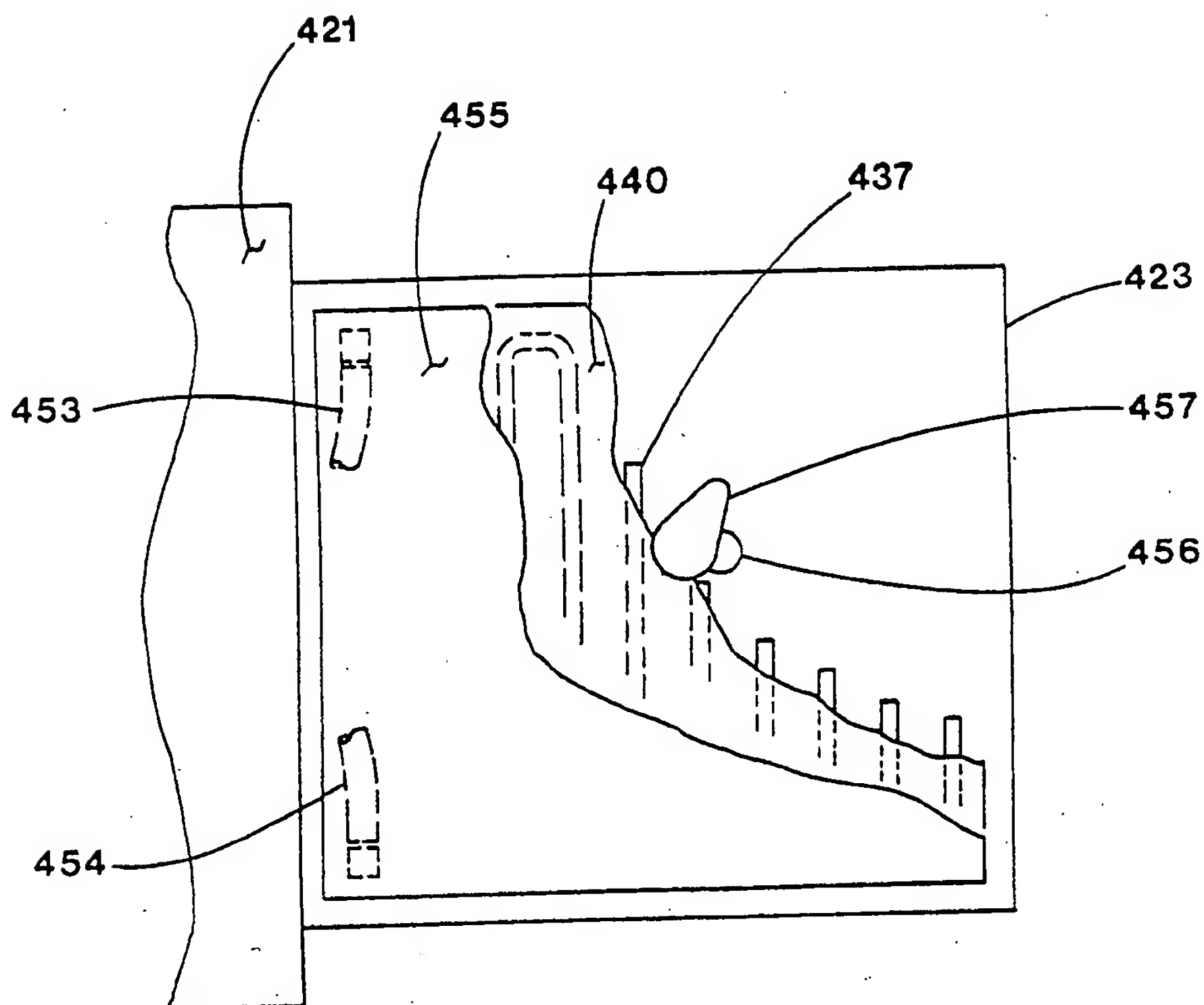
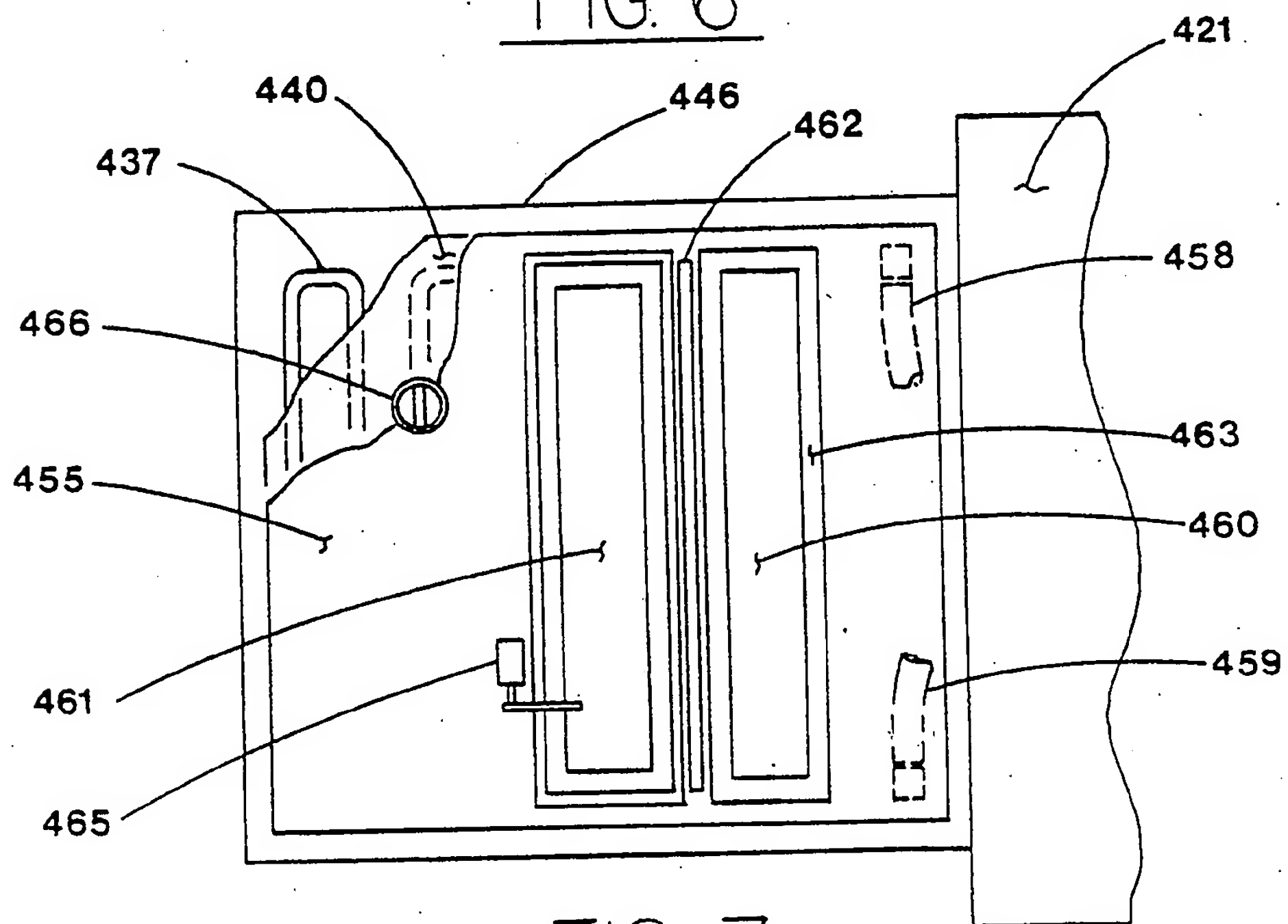


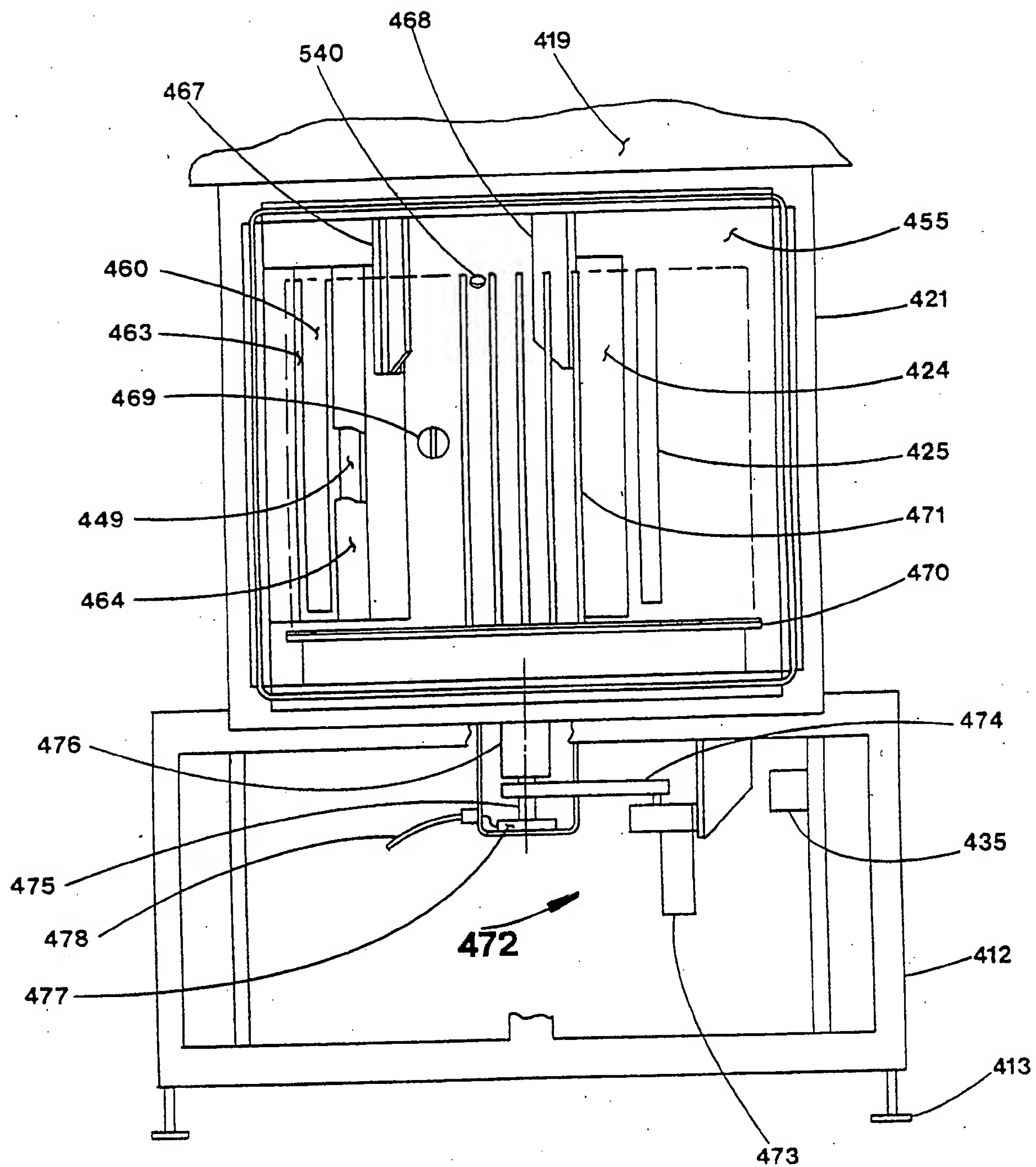
FIG. 3

FIG. 4

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FIG. 5

FIG. 6FIG. 7

FIG. 8



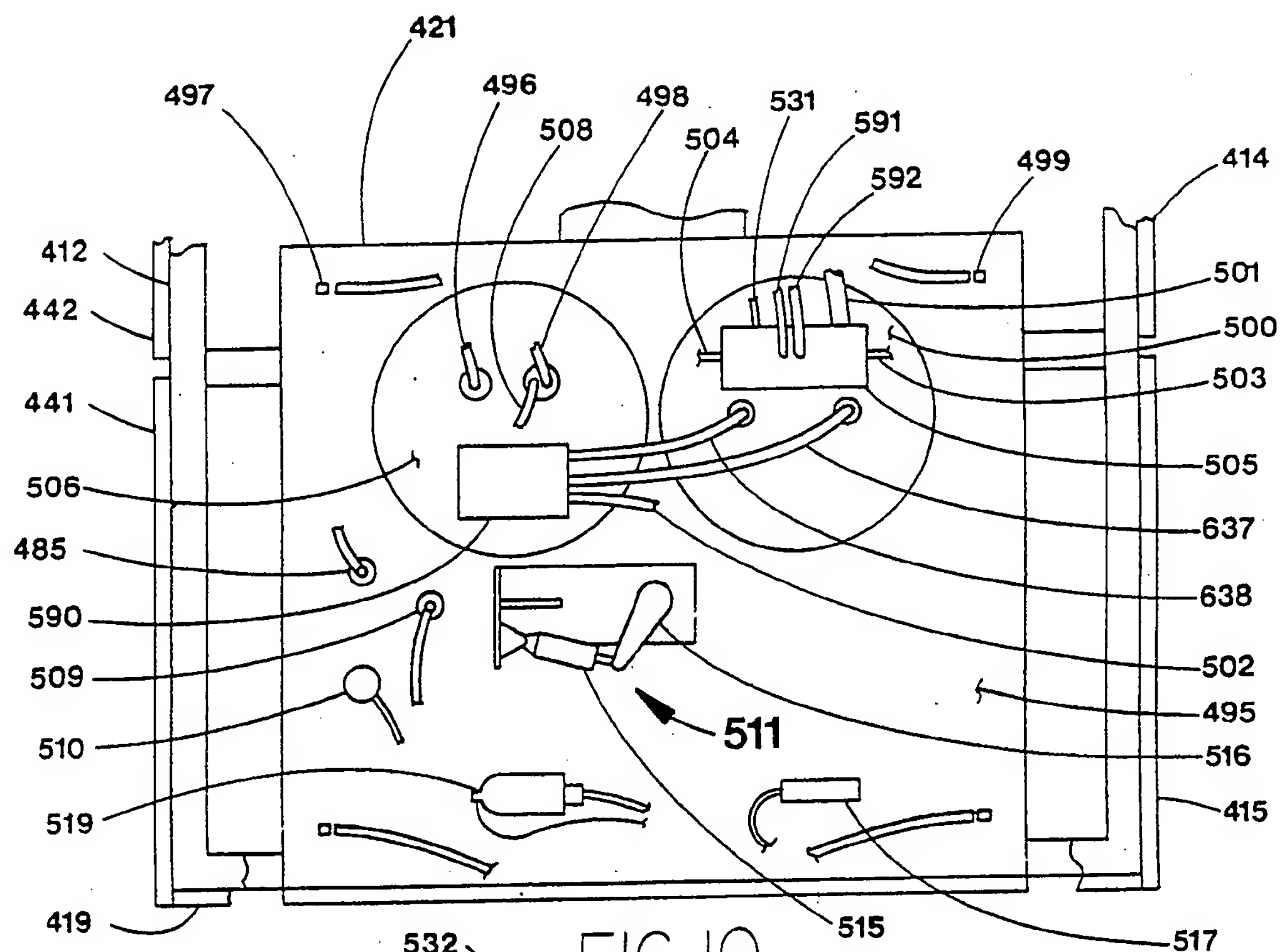


FIG. 10

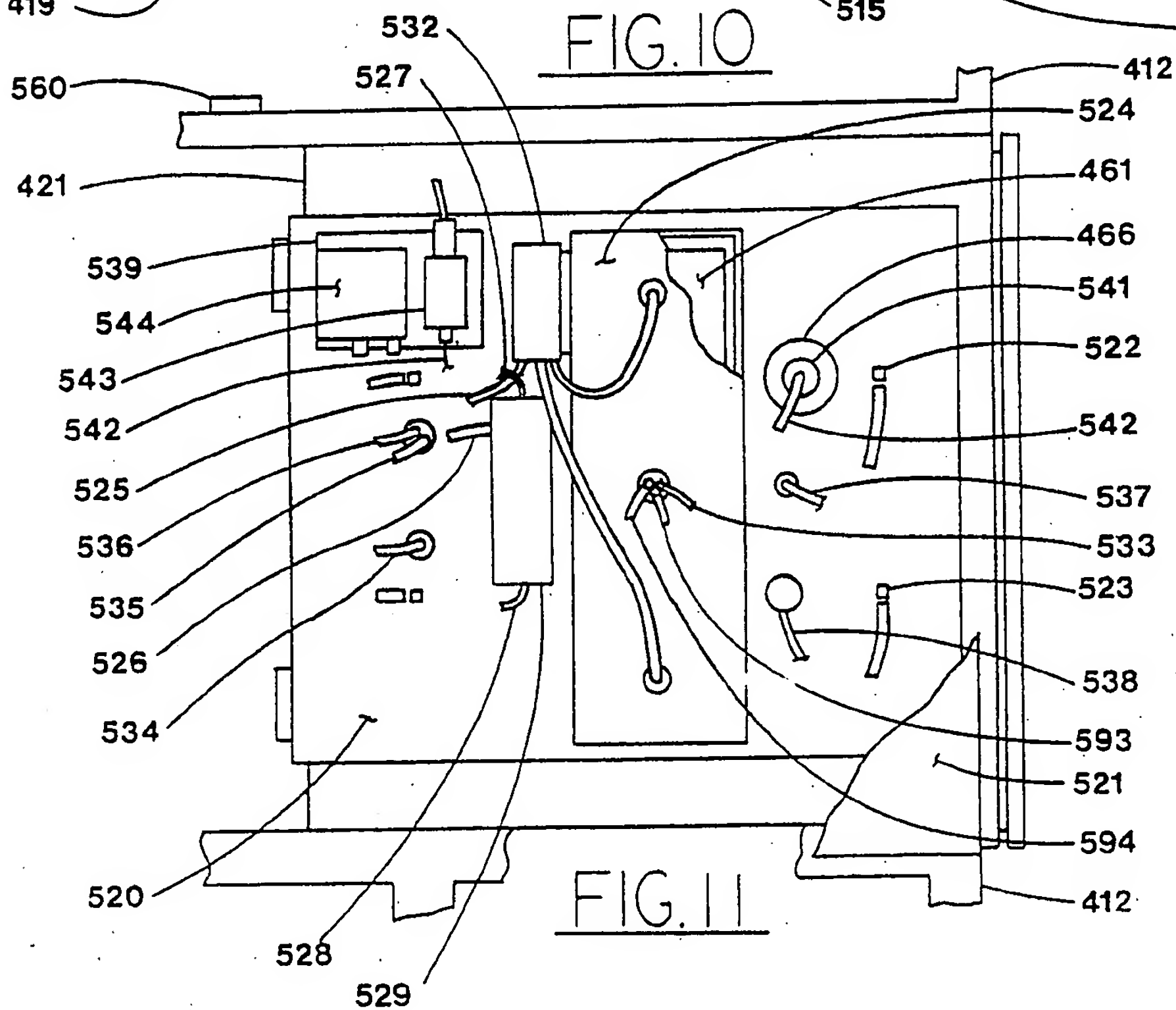
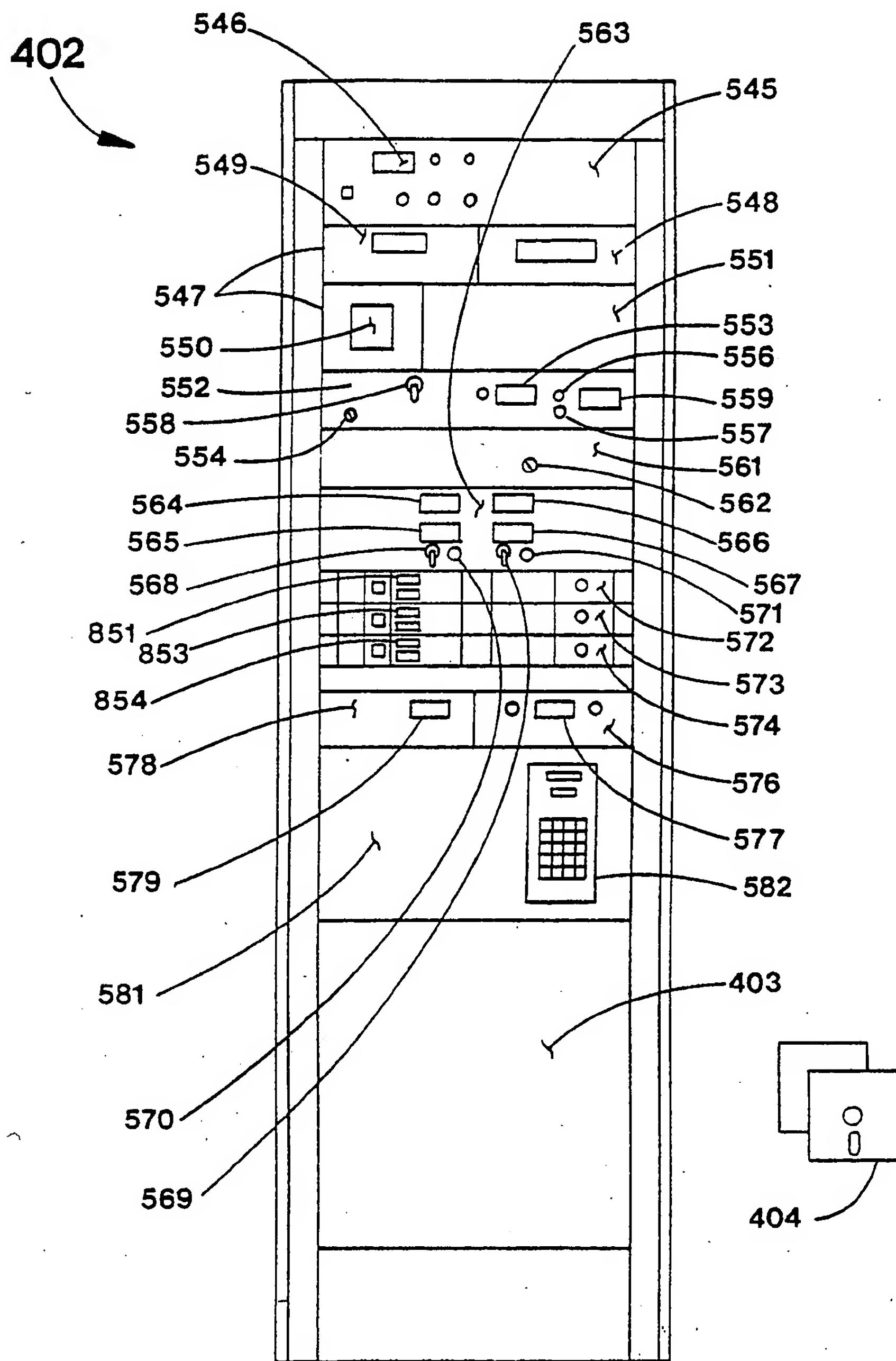


FIG. 11

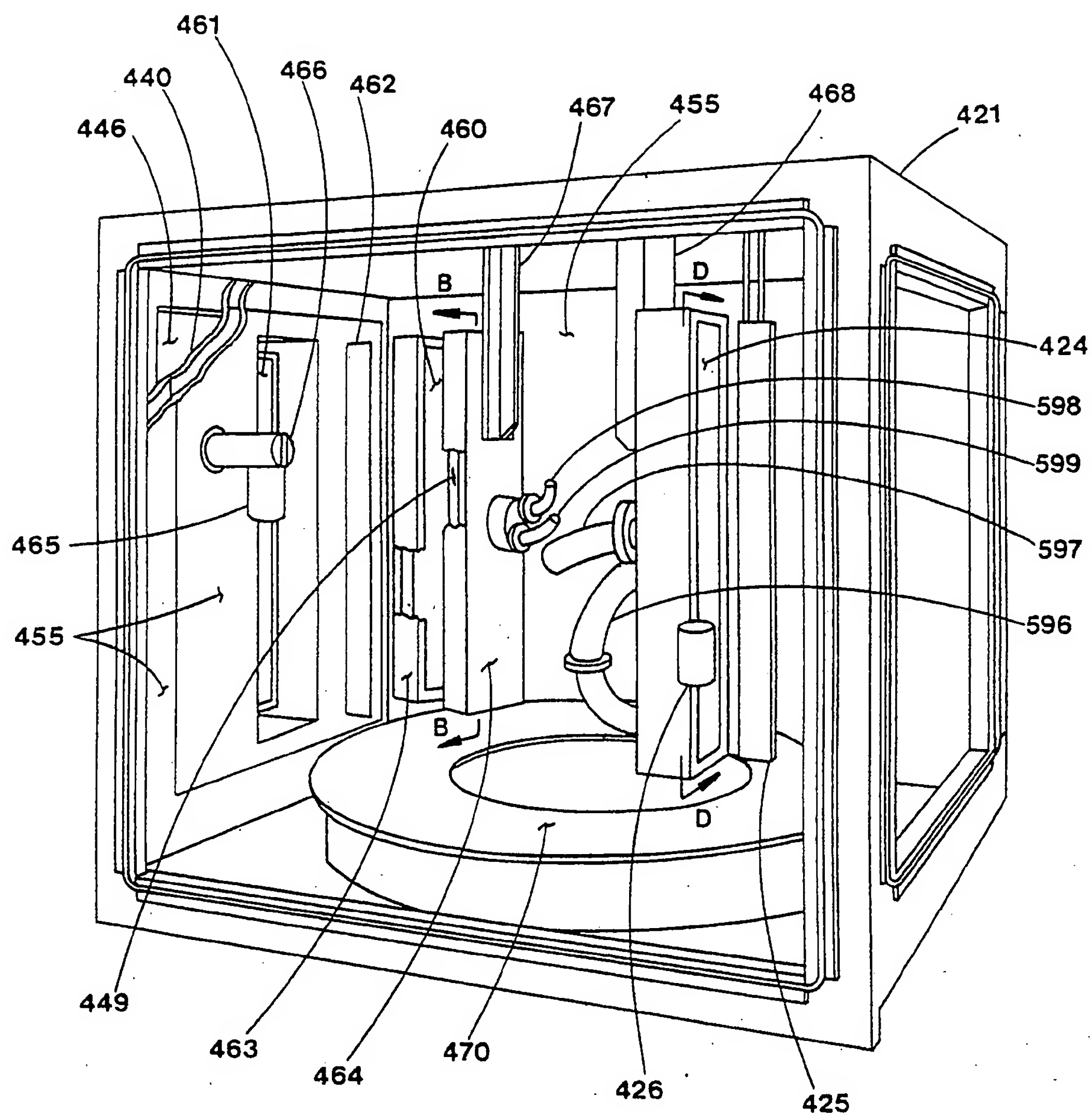
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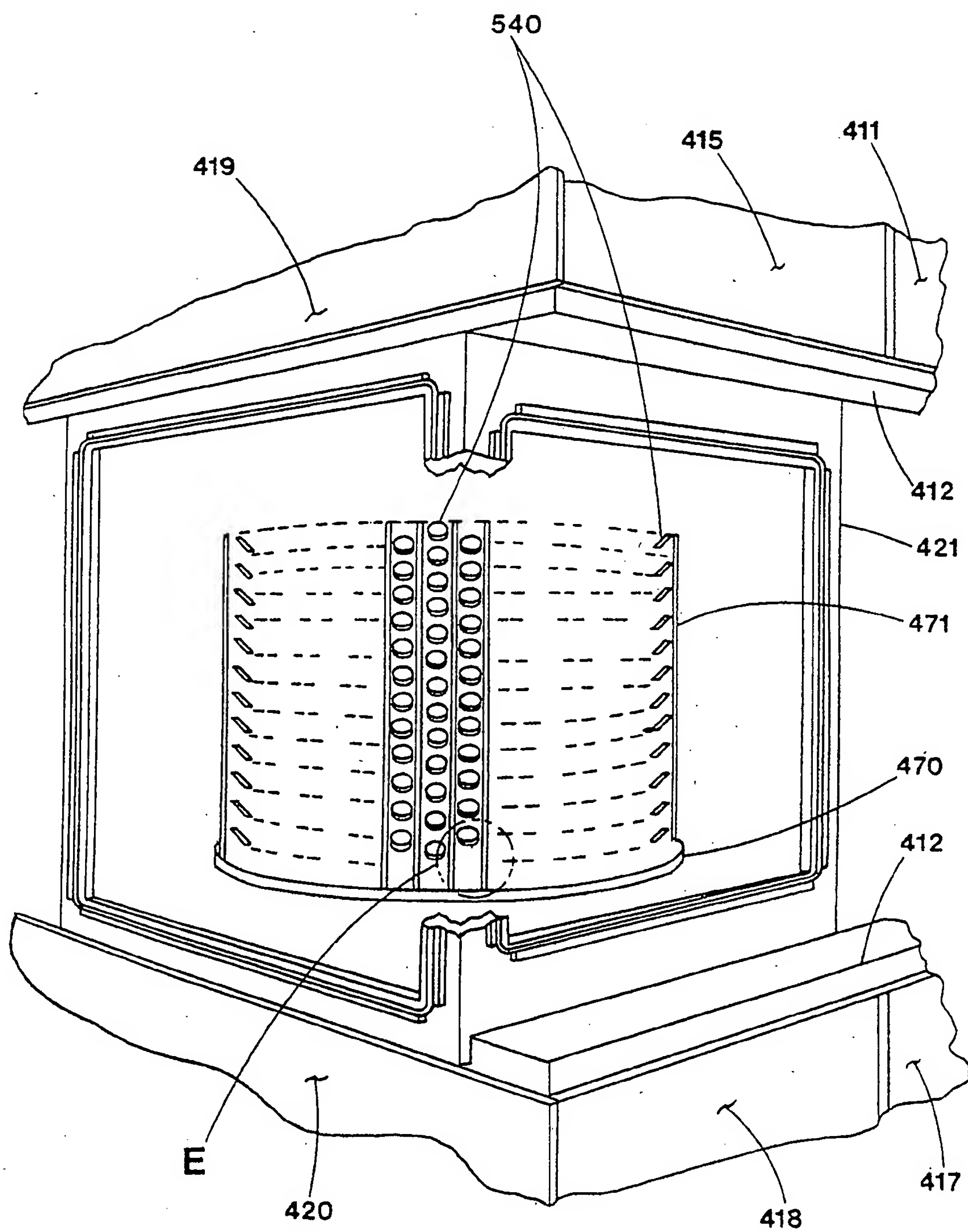


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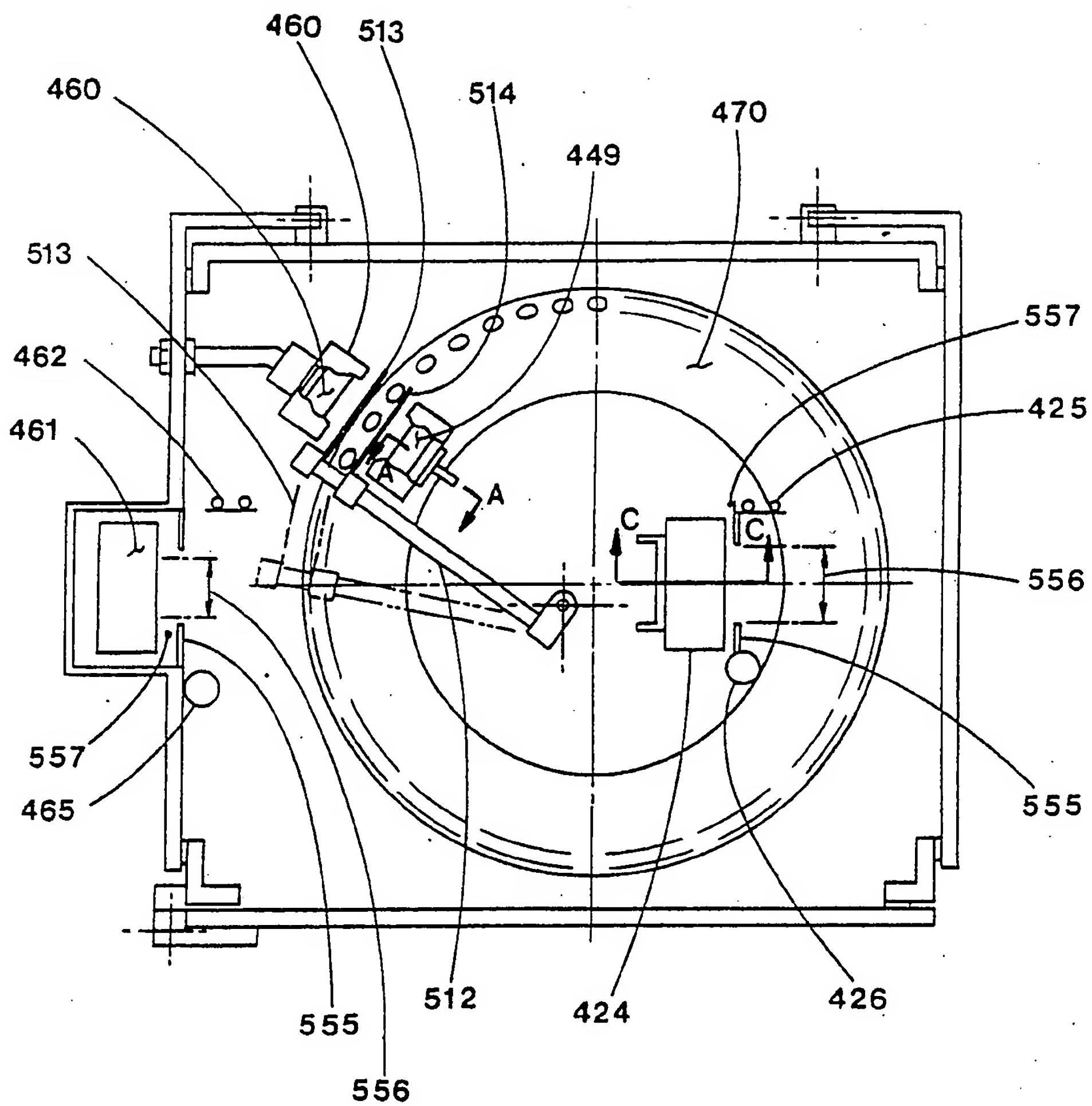
FIG. 12

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FIG. 13

FIG. 14

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FIG. 15

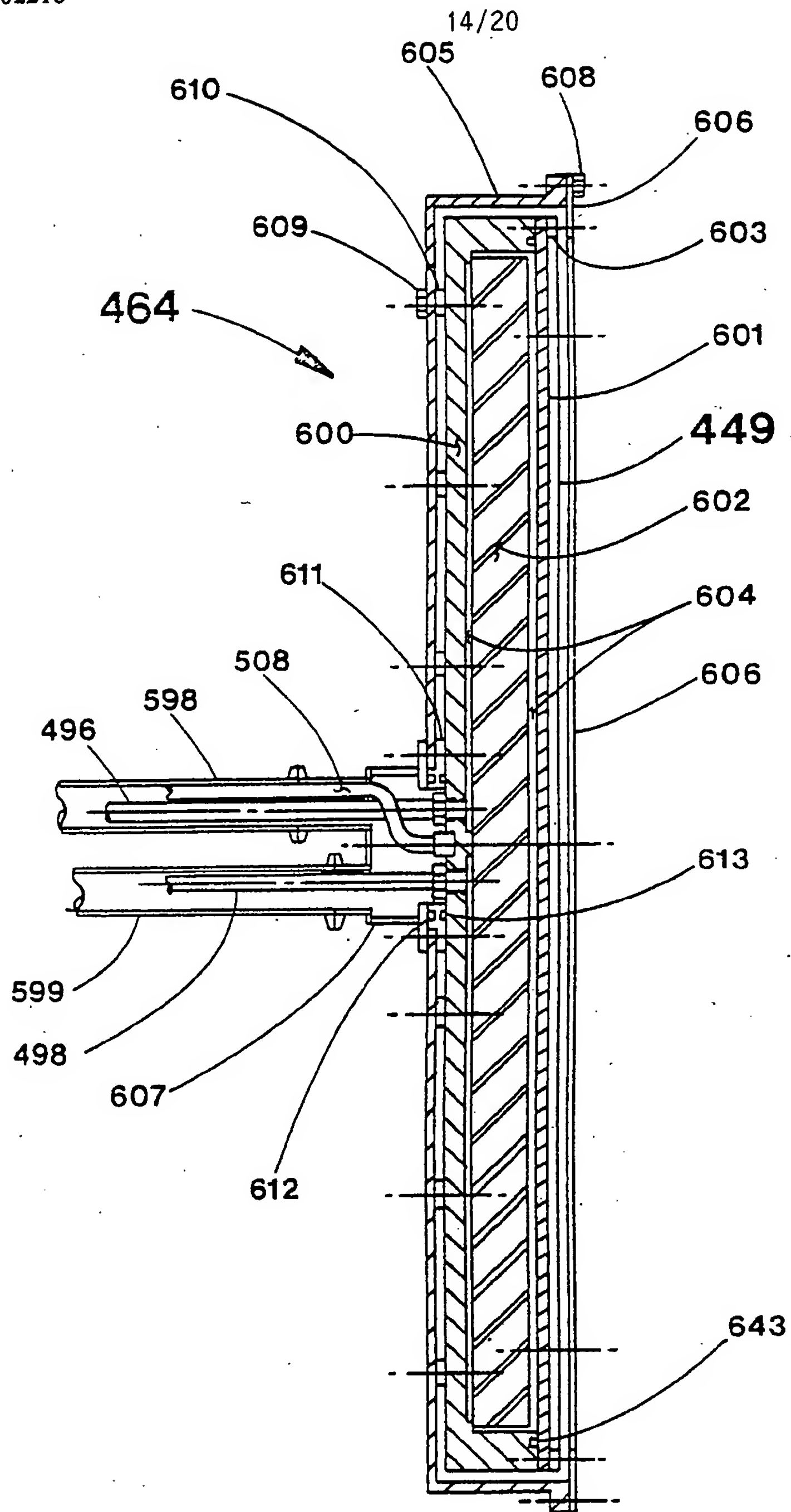


FIG. 16

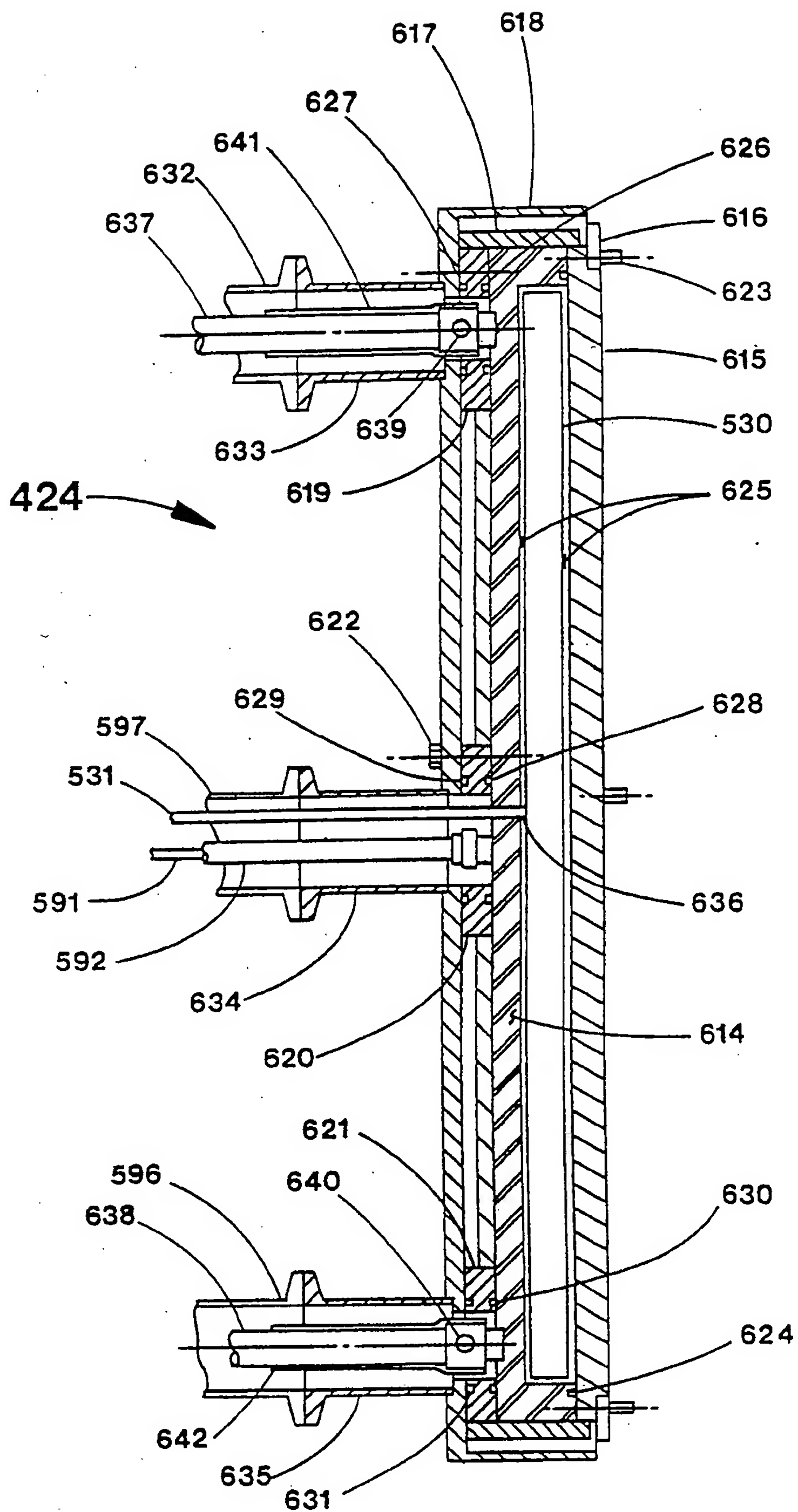


FIG. 17

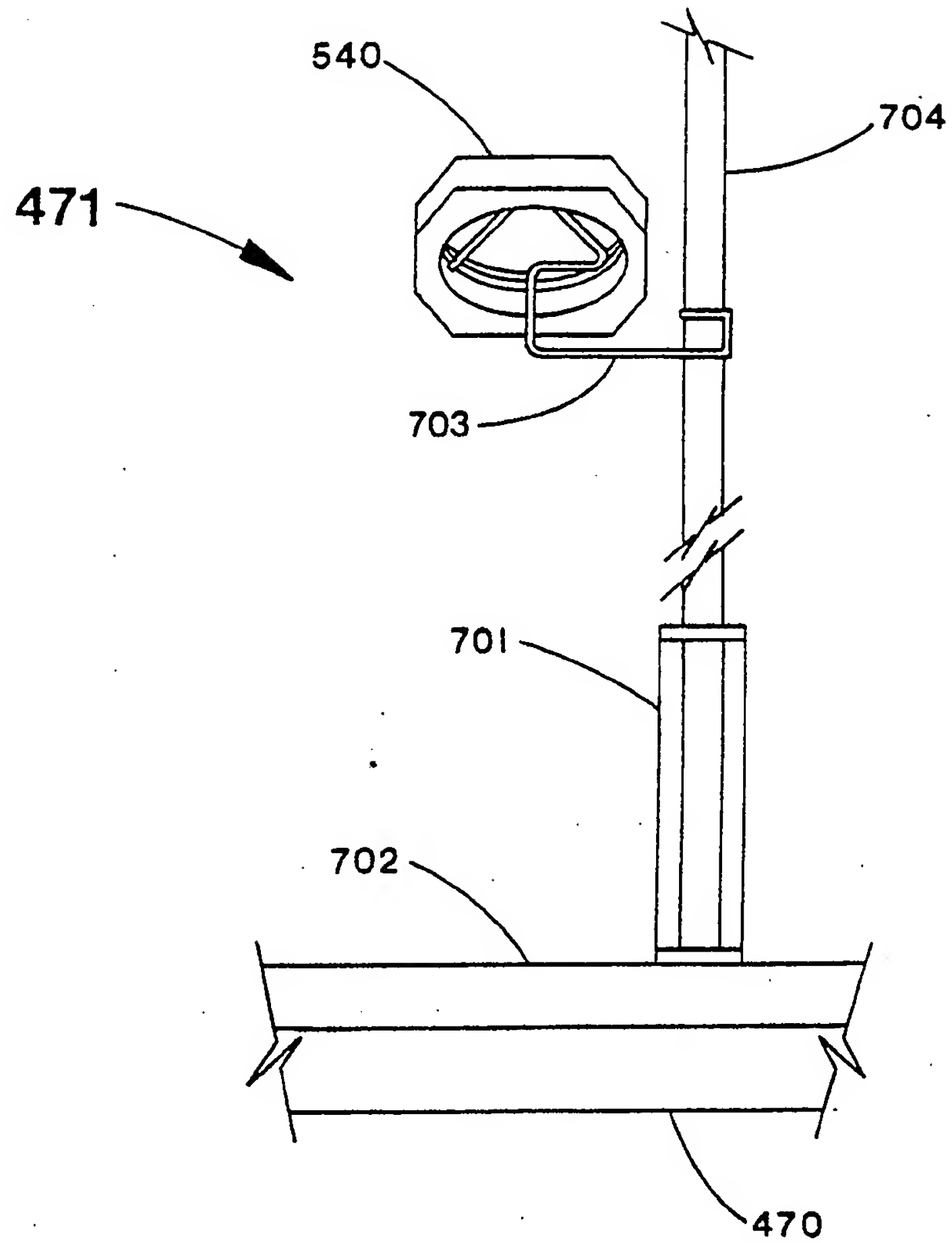
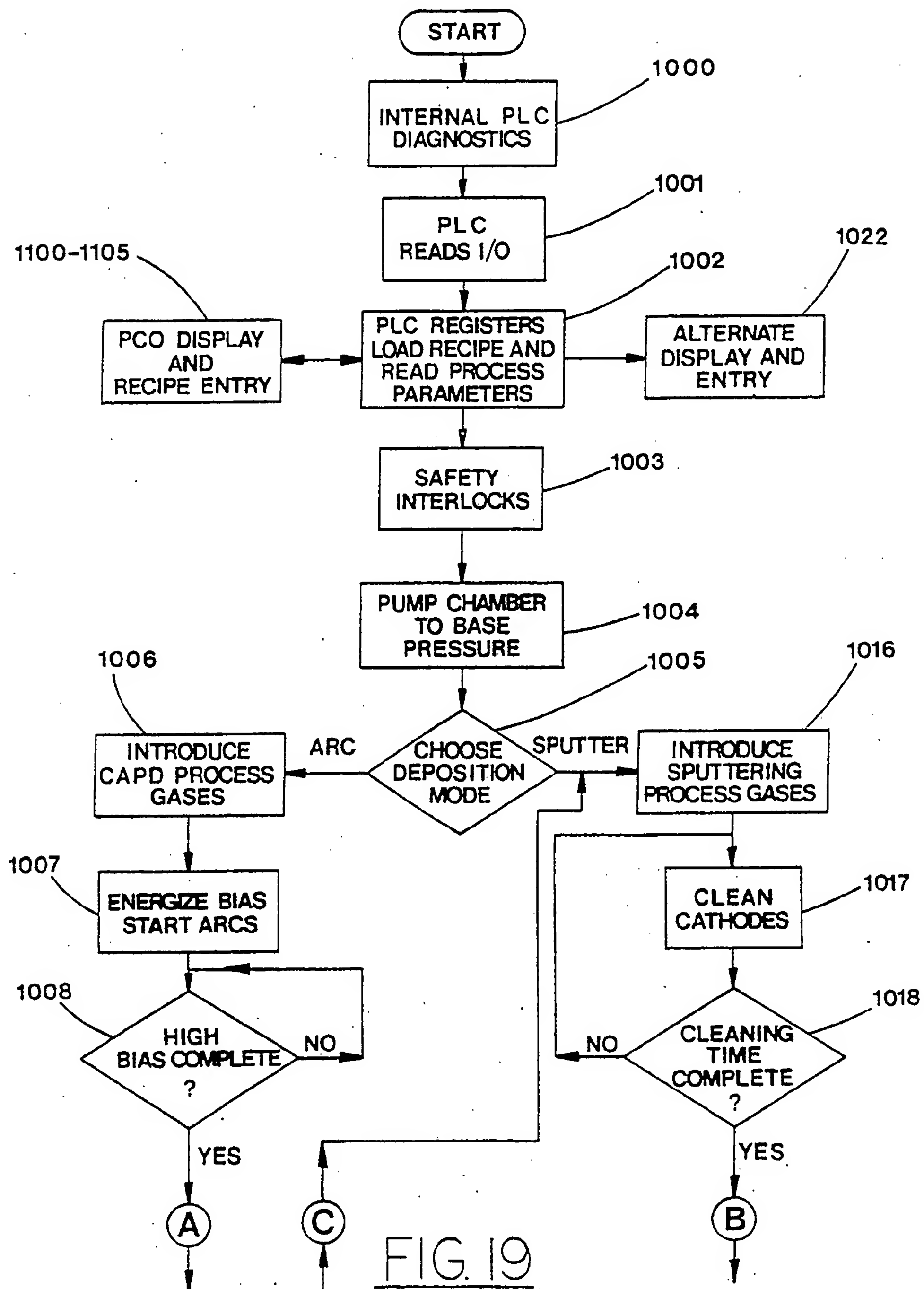
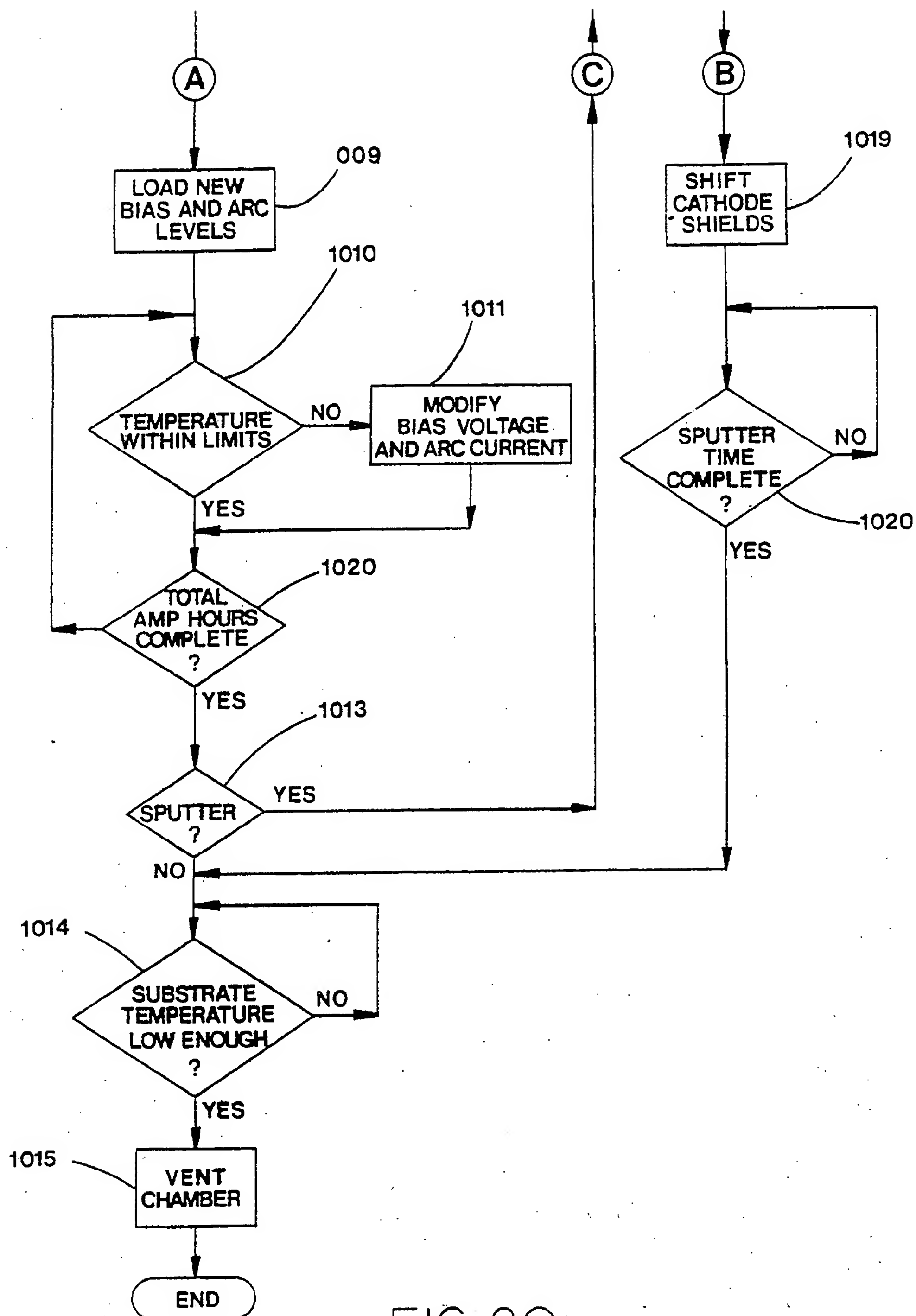
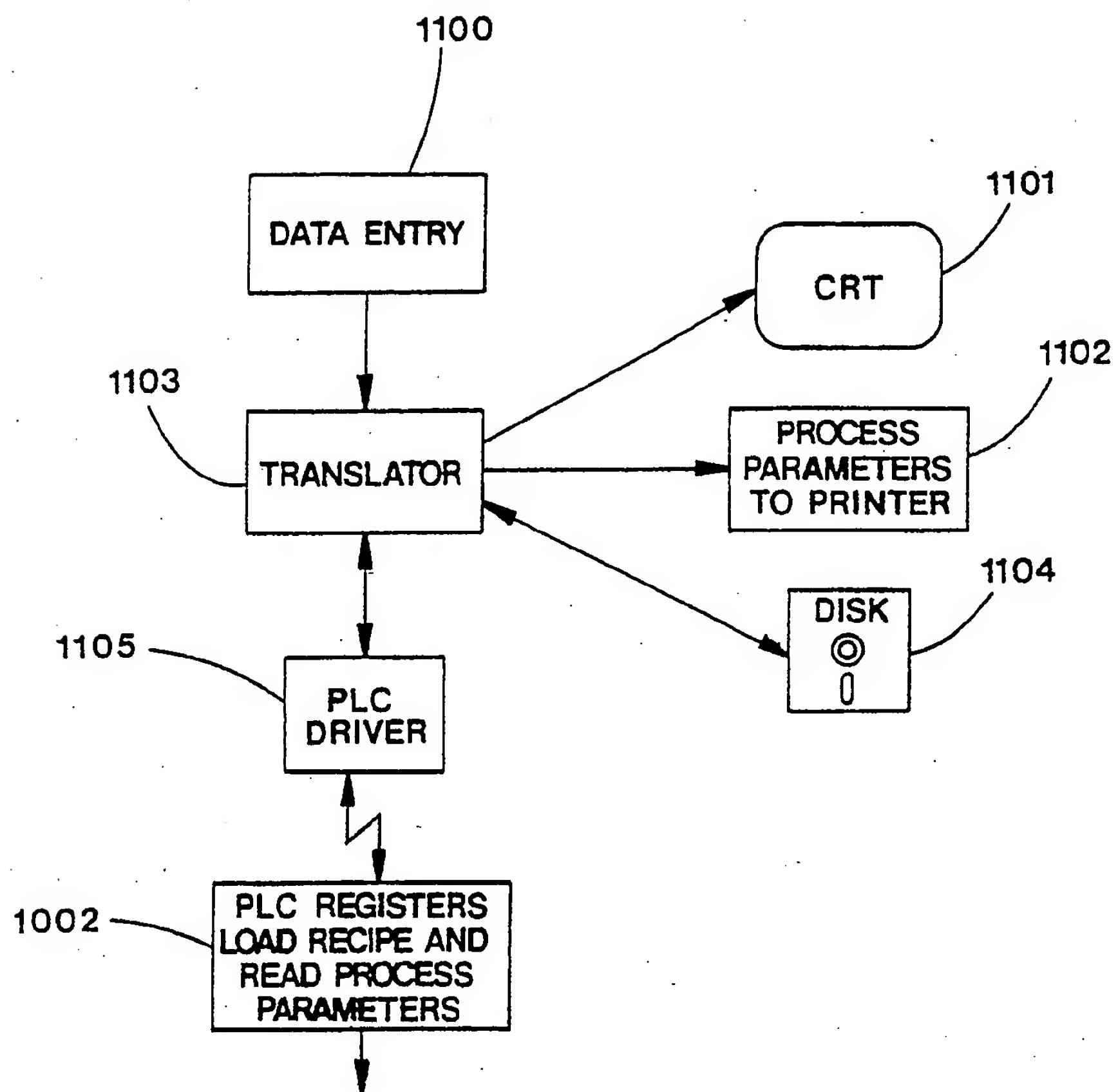


FIG. 18





FIG. 20

FIG. 21

S.No.	COMPOSITION	RANGE		
		L	a	b
1	TiN	77-80	2-5	33-37
2	TiC <sub>0.05</sub> N <sub>0.95</sub>	76-79	5.5-8	30-33
3	TiC <sub>0.10</sub> N <sub>0.90</sub>	71-75	8.5-11	23-28
4	TiC <sub>0.15</sub> N <sub>0.85</sub>	66-69	11-16	21-22
5	ZrN	86-89	-3--1	23-25
6	ZrC <sub>0.10</sub> N <sub>0.90</sub>	81-84	-1--0.4	26-29
7	ZrC <sub>0.15</sub> N <sub>0.85</sub>	79-81	0-3	17-19
8	Gold 10K	81-86	-1.6-1	19-30
9	Gold 24K (Pure)	88-91	-3.7-1	27-34

FIG. 22

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US88/02950

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>4</sup> C23C 14/34; C23C 14/54 U.S. CL. 204/192.38, 298; 364/500		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
U.S.	204/192.12, 192.13, 192.15, 192.16, 192.17, 192.38, 298MT, 298CS, 298MS, 298PM, 298MC, 298MD, 298D 364/500	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>*</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	US,A, 4,234,622 (DU BUSKE ET AL) 18 November 1980	1-38, 40-46
A	US,A, 4,560,462 (SNYDER) 27 May 1988	1-38, 40-46
A	US,A, 4,648,952 (HERKLOTZ ET AL) 17 January 1989	1-38, 40-46
A	US,A, 4,500,408 (BOYS ET AL) 19 February 1985	39
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>*</sup> Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the International filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the International filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of International Search Report
April 10, 1989		<div style="border: 1px solid black; padding: 2px; display: inline-block;"> <b>7 MAY 1989</b> </div>
International Searching Authority		Signature of Authorized Officer
ISA/US		Aaron Weisstuch